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FINAL RESEARCH REPORT ON SECTION B

CONTRACT NCMR 807(00)

SODIUM PERCHLORATE

This document has been reviewed in accordance with
OPNAVINST 8510.17, November 1953. The security
classification assigned herein is correct.

Date: 1/5/54

By direction of *J. W. Gutz*
Chief of Naval Research (Code 425)

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PENNSYLVANIA SALT MANUFACTURING CO.

OFFICE OF NAVAL RESEARCH PROJECT NR 352-304/2-1-52 (CONTRACT NONR 807(00))

SODIUM PERCHLORATE: Research Leading Toward the
Development of Selected Methods to Produce Sodium
Perchlorate Without the Use of Platinum

FINAL RESEARCH REPORT ON SECTION B:
Disproportionation of Sodium Chlorate
in Acid Solution.

by

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August 25, 1953

Pennsalt Project 4-00048-60
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SUBJECT

Sodium Perchlorate: Research Leading Toward the Development of Selected Methods to Produce Sodium Perchlorate Without the Use of Platinum (Project Number NR 352-304/2-1-52; Contract Number NCMR-807(00)).

OBJECT

To investigate methods for production of sodium perchlorate without the use of platinum; to include, but not necessarily be limited to, the following:

- (1) The use of anodes comprising silicon-silicon carbide
- (2) The use of lead dioxide coated anodes
- (3) The disproportionation of sodium chlorate in acid solution

SCOPE

This Final Research Report, labeled Section B, covers all work done on the disproportionation of sodium chlorate in acid solution including that done under Project NR 352-263/2-10-51 and the present Project NR 352-304/2-1-52.

The electrochemical work with anode materials, the authorization for which has been extended to January 31, 1954, is being covered in separate periodic progress reports.

SUMMARY

1. A 30% to 33% conversion of sodium chlorate to sodium perchlorate has been attained in both a batch and continuous type process, using 70% sulfuric acid at 93°C., or with 83% acid at 69°C. This is 90-99% of theory, assuming disproportionation of chlorate to perchlorate and chlorine dioxide.
2. The yield of chlorine dioxide in the disproportionation of chlorate varied from 25% with 70% sulfuric acid, to 88% with 83% acid. The remainder of the gas was substantially chlorine.
3. The chlorine dioxide-chlorine mixtures were readily absorbed in 100 to 200 g/l caustic solution and the resulting mixture of chloride, hypochlorite, chlorite, and chlorate were reconverted to chlorate by electrolysis in a chlorate type cell.
4. The reaction between chlorite and hypochlorite to form chlorate and chloride and the disproportionation of chlorite to chlorate and chloride were also studied as possible methods of recovering chlorate from the above mixtures.
5. The use of perchloric acid in place of sulfuric acid in the disproportionation of sodium chlorate resulted in comparable conversions of sodium chlorate to perchlorate in batch type reactions.
6. Perchlorate values have been recovered from the sulfuric acid disproportionation reactions either as ammonium and potassium perchlorates by a fractional crystallization method, or as perchloric acid by a vacuum distillation. The vacuum distilled perchloric acid could be converted to a high purity ammonium perchlorate by reaction with anhydrous ammonia. When perchloric acid was used in this process, sodium perchlorate was recovered by direct crystallization.

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7. Approximately 1/2 pound samples of potassium and ammonium perchlorate have been made in single laboratory preparations.

8. No catalyst was found that would change the course or the speed of the disproportionation reactions.

9. The by-product in the 83% sulfuric acid process was a solid complex of sodium acid sulfate, sulfuric acid and water of hydration containing 63% by weight of equivalent sulfuric acid values.

10. A projected continuous cyclic process using 83% sulfuric acid was developed on which to base a cost estimate, and as a preliminary guide for pilot or industrial scale development of the disproportionation process.

11. A cost estimate on the production of 10,000 TPY of potassium perchlorate by the disproportionation process gave a cost of 20.2¢ per pound, assuming that the by-product acid mixture is sold at its sulfuric acid value. On the same basis, the cost of potassium perchlorate by the electrolytic method using platinum anodes would be 14.0¢ per pound.

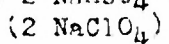
12. A cost estimate on the production of 10,000 TPY ammonium perchlorate by the disproportionation process gave a cost of 21.5¢ per pound, assuming that the by-product acid mixture is sold at its sulfuric acid value. This is based on forming the ammonium perchlorate by vacuum distilling perchloric acid from the acid disproportionation mixture, and reacting it with anhydrous ammonia.

13. An analytical procedure was developed for mixtures containing perchlorate, chlorate, chlorite, hypochlorite and chloride. On testing this procedure, analytical results duplicated actual sample compositions to within 1.5%.

14. A patentability and infringement study has been completed on the projected process.

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potassium perchlorate

RECOMMENDATIONS

1. If an alternate to the electrolytic process using conventional or alternate anodes is desired, the acid disproportionation process should be compared with other chemical methods now being studied and the most promising one chosen for pilot plant testing.
2. The choice of acids should be made on the basis of the relative degree of hazard involved and usefulness of the by-products.
3. Patent application should be filed on the novel points of the acid disproportionation process.

LABORATORY STUDY

A. Disproportionation of Sodium Chlorate in Acid Solution

1. Summary of Previous Work done Under 1951 Project NR 352-263/2-19-51.

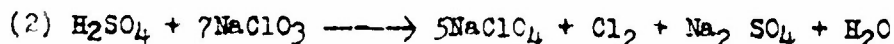
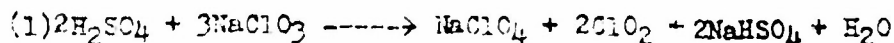
The 1951 laboratory work was of a limited exploratory nature which simply established that appreciable yields of sodium perchlorate could be obtained on reacting sodium chlorate and sulfuric acid. It was recognized that a patented process(1) for making perchlorates and chlorites of different metals by the above reaction would be of doubtful value. However, it was felt that an adaptation of this process which did not recover chlorite, but returned all reduced chlorate to a chlorate cell to be reconverted might be practical.

2. Reaction Study

a. Pot Reactor

The purpose of this phase of the work was to determine the feasibility of and the optimum conditions for the production of perchlorates by the disproportionation reaction of a chlorate such as sodium chlorate in a concentrated strong acid. The major part of our effort has been in reactions with sulfuric acid, although a few preliminary experiments were carried out with perchloric acid.

Numerous reactions might seem possible, depending on reactant concentrations, temperature, etc. between the limits of the two following equations:



The evidence of this research, however, as discussed in a later part of this section, is that equation (1) shows the only course of reaction under the conditions used in this research, although chlorine may also be formed by the partial vapor phase thermal decomposition of chlorine dioxide. A 33.3% conversion of sodium chlorate to perchlorate represents the theoretical maximum yield by equation 1. As expected, the recovery of oxidizing chlorine values in the off-gases was found to require considerable research effort.

Sodium chlorate was introduced into the reaction as a concentrated solution, 650 gms./l. This was found to be very satisfactory and much preferable to the use of solid sodium chlorate, which results in violent local reaction. In a series of preliminary experiments, the sulfuric acid was held in an open pyrex vessel, and the sodium chlorate solution was added dropwise. When all the sodium chlorate had been mixed in with the acid, the temperature of the mixture was raised to the desired point (60°-100°C.) and digested for periods of 1/2 to 5 hours. The solution was flushed at all times with nitrogen gas introduced through a fritted glass gas washing tube.

The reaction of 50% sulfuric acid with sodium chlorate solution was too slow and mild. Using 70% sulfuric acid, promising yields were obtained in the temperature range of 70° - 100°C. with a 3 hour reaction period. Use of 83% sulfuric acid yielded more perchlorate than 70% acid under approximately the same conditions, but with precipitation of some solids at room temperature. The reaction of 96% sulfuric acid with the concentrated sodium chlorate solution tended to be violent and resulted in the immediate precipitation of a considerable amount of solids at or near room temperature. These solids dissolved at about 70°C., but heavy foaming of the reaction mixture occurred at this elevated temperature. Although the yield from one experiment with 96% sulfuric acid was good, it was decided to carry out further work with the 70% and 83% acid. In these preliminary experiments, conversions of sodium chlorate to perchlorate in excess of 32% were reached.

In order to determine, in further experiments with sulfuric acid, whether any perchloric acid was being distilled out of the reactor during the heating of the chlorate-acid mixture after they had been mixed at room temperature, and, also, to determine the composition of the reactor vapors, especially in regard to oxidizing power, a closed reaction vessel was used. The reactor vapors were flushed out with nitrogen and absorbed in a train of two 8% sodium hydroxide solutions of 125 mls. each. The reaction mixtures, except as otherwise noted, consisted of 50 mls. of sulfuric acid of given strength and 38.5 mls. of a 650 gms./l. NaClO_3 solution (25 gms. NaClO_3). For 70% acid this gave an $\text{H}_2\text{SO}_4/\text{NaClO}_3$ weight ratio of 4.1, and for 83% acid, the ratio was 5.3. The following variables affecting the degree of conversion of sodium chlorate to perchlorate were studied with 70% and 83% sulfuric acid: (1) reaction temperature, and (2) ratio of acid to chlorate.

The reactions with 70% acid were carried out at 69° and 93°C. with reaction periods of 3 to 6 hours. At 69°, the conversion of sodium chlorate to the perchlorate fell in the range of 11 to 22% for the above respective reaction times. At 93°C. the yield was about 32%, practically independent of reaction time. The conversion of sodium chlorate to the perchlorate at 69°C. when using 83% sulfuric acid ranged from 29 to 33% for reaction periods of 3 to 6 hours respectively. Attempts to heat a mixture of 83% sulfuric acid and concentrated sodium chlorate solution to 93°C. resulted in moderate explosions at about 78°-80°C. At these temperatures the concentration of yellow chlorine dioxide in the reactor vapor space increased too rapidly to be carried away by any practicable flow of nitrogen. These results are outlined in Tables I and II.

From analyses of the absorber solutions for oxidizing power and chlorine content, the composition of the reactor vapors was calculated and expressed as per cent chlorine and chlorine dioxide. With 70% acid reacted at 69°C., the composition of the reactor vapors could be considered as 100% ClO_2 , and when the reaction temperature was raised to 93°C., the ClO_2 content dropped to 33% (77% Cl_2).

When reacting 83% sulfuric acid with sodium chlorate solution and heating to 69°C., the ClO_2 content of the absorbed reactor vapors ranged from 33 to 35% (12 to 15% Cl_2) for reaction periods of 3 to 6 hours respectively. These results are given in Tables III and IV.

As the ratio of the weight of equivalent 100% H_2SO_4 to the weight of equivalent solid sodium chlorate was increased from 2.6 to 8.1 when reacting 70% acid at 93°C., the conversion of sodium chlorate to the perchlorate rose from 28 to 33%. At the same time the ClO_2 content of the absorbed reactor vapors dropped from 48 to 23% (52 to 77% Cl_2). When reacting 83% acid in the acid-chlorate ratio range of 3.4 to 10.5, from 31 to 33% of the sodium chlorate was converted to perchlorate respectively at 69°C. Under these conditions, the absorbed reactor vapors ranged in composition from 93 to 84% ClO_2 (7 to 16% Cl_2). The reaction period for all experiments in this series was 4.5 hours. Tables V and VI show these results.

In interpreting the above yields, it should be noted that for a reaction exactly following equation (1) (Page 5) in which chlorine dioxide is the only oxidizing gas given off, a 33.3% conversion of sodium chlorate to perchlorate represents the maximum possible yield, while for equation (2) where chlorine is the only oxidizing gas given off, a 71.4% conversion represents the maximum possible yield. In most of the above experiments in which the reaction of sulfuric acid and sodium chlorate was carried out, a considerable amount of chlorine dioxide was found in the absorber solutions. Thus, the yields might be expected to be closer to the value for equation (1). Even in those cases where the reactor gases as absorbed in sodium hydroxide solution are analyzed as having been to a large degree chlorine, it is likely that the gases just as they evolved from the reactor solution were chlorine dioxide. Brown (2) has found that in the gas phase, chlorine dioxide undergoes thermal decomposition into chlorine and oxygen. This reaction rate rises rapidly with temperature, especially above 60°C. In aqueous solution, chlorine dioxide may undergo catalytic hydrolysis into chloric and hydrochloric acids. If no catalyst is present, the solutions are stable, even at 96.5°C.

Distillation or carry over as mist of perchloric acid from the reactor was found to be negligible at the reaction temperatures used (93°C. max.).

During the course of these experiments the observation was made that as the mixture of 70% sulfuric acid and concentrated sodium chlorate solution is heated, there is a continuous evolution of strongly yellow vapors until the temperature reaches 90°-93°C., at which point the evolution of the yellow vapors stops sharply. For 83% sulfuric acid, this characteristic temperature is 67-69°C. These then were considered to be the desirable temperatures for carrying out the formation of perchlorate, since at lower temperatures, the reaction rate is very slow, and at higher temperatures,

TABLE I

Effect of Acid Strength on Yield of Sodium Perchlorate in

 $\text{NaClO}_3\text{-H}_2\text{SO}_4$ Reaction

(Pot Reactor)

STRENGTH OF H_2SO_4 USED wt. %	LENGTH OF DIGES- TION PERIOD - HOURS	WT. OR MOL % OF NaClO_3 CONVERTED TO NaClO_4
70	3.0	10.8
	4.5	15.6
	6.0	22.0
83	3.0	29.5
	4.5	31.3
	6.0	33.4

Reaction Temperature (ave. max.) = 69°C .

Reaction Charge: 90 mls. of H_2SO_4 of given strength
28.5 mls. of NaClO_3 solution, 650g.
 NaClO_3 /liter.

TABLE II

Effect of Reaction Temperature on Yield of Sodium Perchlorate
in $\text{NaClO}_3\text{-H}_2\text{SO}_4$ Reaction
(Pot Reactor)

REACTION TEMP. °C.	LENGTH OF DIGES- TION PERIOD HOURS	WT. OR MOL % OF NaClO_3 CON- VERTED TO NaClO_4
69	3.0	10.8
	4.5	15.6
	6.0	22.0
93	3.0	32.1
	4.5	30.9
	6.0	33.0

Reaction Charge: 90 mls. of 70% H_2SO_4
38.5 mls. of NaClO_3 solution, 650g.
 $\text{NaClO}_3/1.$

TABLE III

Effect of Acid Strength on Composition of Reactor Vapors Formed
in $\text{NaClO}_3\text{-H}_2\text{SO}_4$ Reaction
(Pot. Reactor)

(Values given are totals found in both caustic absorber
solutions used in absorbing train.)

STRENGTH OF H_2SO_4 USED WT. %	LENGTH OF DIGESTION PERIOD HOURS	TOTAL WT.* OF Cl IN ABSORBING SOLUTIONS GMS.	% OF Cl AS Cl_2	% OF Cl AS ClO_2
70	3.0	1.91	None	100
	4.5	2.00	None	100
	6.0	3.20	0.6	99.4
83	3.0	5.50	11.8	88.2
	4.5	5.46	12.4	87.6
	6.0	5.56	14.7	85.3

* - Weight of Cl per 25 grams of NaClO_3 charge

Reaction Temperature (ave. max.) = 69°C .

Reaction Charge: 90 mls. of H_2SO_4 of given strength
38.5 mls. of 650g./l. NaClO_3

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TABLE IV

Effect of Reaction Temperature on Composition of Reactor Vapors
Formed in $\text{NaClO}_3\text{-H}_2\text{SO}_4$ Reaction.

(Pot Reactor)

(Values given are totals found in both caustic absorber
solutions used in absorbing train.)

REACTION TEMP. (AVE. MAX.) °C.	LENGTH OF DIGESTION PERIOD HOURS	TOTAL WT.* OF Cl IN ABSORBING SOLUTIONS GMS.	% OF Cl AS Cl_2	% OF Cl AS ClO_2
69	3.0	1.91	None	100
	4.5	2.00	None	100
	6.0	3.20	0.6	99.4
93	3.0	4.17	75.1	24.9
	4.5	4.70	76.2	23.8
	6.0	4.94	76.7	23.3

* Weight of Cl per 25 grams of NaClO_3 charge

Reaction Charge: 90 mls of 70% H_2SO_4
38.5 mls of 650 g./l. NaClO_3

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TABLE V

Effect of Ratio of Sulfuric Acid to Sodium Chlorate on Yield
of Sodium Perchlorate.

(Pot Reactor)

Strength of H_2SO_4 Used Wt. %	Ratio: Wt. of Equiv. 100% H_2SO_4 Vs. Wt. of $NaClO_3$	Wt. or Mol % of $NaClO_3$ Converted to $NaClO_4$
70	2.6	27.8
	4.1	30.0
	8.1	36.3 *
83	3.4	31.2
	5.3	31.3
	10.5	34.9 *

Length of Digestion Period - 4.5 hours

Reaction Temp. (ave. max.)

93°C (when using 70% H_2SO_4)

69°C (when using 83% H_2SO_4)

- * - A 33.3% conversion of sodium chlorate to perchlorate represents the theoretical maximum yield by equation 1 of Page 5. These results were obtained before extended refinements in analytical procedures for mixtures of chlorate and perchlorate

TABLE VI

Effect of Ratio of Sulfuric Acid to Sodium Chlorate on Composition
of Reactor Vapors

(Pot Reactor)

(Values given are totals found in both caustic absorber solutions
used in absorbing train.)

Strength of H_2SO_4 Used Wt. %	Ratio Wt. of Equiv. 100% H_2SO_4 Vs. Wt. of $NaClO_3$	Total Wt.* of Cl in Absorbing Solutions gms.	% of Cl as Chlorine	% of Cl as Chlorine Dioxide
70	2.6	4.26	51.6	48.4
	4.1	4.70	76.2	23.8
	8.1	5.33	77.2	22.8
83	3.4	4.32	7.0	93.0
	5.3	5.46	12.4	87.6
	10.5	5.41	16.4	83.6

* Weight of Cl per 25 grams of $NaClO_3$ Charge.

Length of Digestion Period - 4.5 hours

Reaction Temp. (ave.max.):

93°C (when using 70% H_2SO_4)

69°C (when using 83% H_2SO_4)

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all the chlorine dioxide tends to be thermally decomposed into chlorine and oxygen. When the 83% sulfuric acid and chlorate mixture was heated to 75°C. and higher, there was a reappearance and very rapid increase in concentration of the yellow vapors with the mixture exploding at about 80°C. No attempts were made to carry out any experiments with 70% acid above 93°C. These observations apply to the series of experiments in which the reactor vapors were confined and swept through an absorbing train of caustic solutions by nitrogen bubbled through the reactor solution. In a preliminary experiment in which the reactor was completely open to the atmosphere, a similar mixture of chlorate and 83% sulfuric acid could be heated to 102°C. without exploding.

The reaction of 70% and 83% sulfuric acid with sodium chlorate solution was also carried out by slowly adding the sodium chlorate solution to acid already preheated to the reaction temperature rather than mixing at room temperature and then heating. The yield of sodium perchlorate was not appreciably affected by this change in reaction technique. However, the composition of the evolved reactor vapors was radically changed. With 70% sulfuric acid reacted at 93°C., the chlorine dioxide content dropped from about 25% to 0% (75% to 100% Cl₂), and with 83% sulfuric acid reacted at 69°C., the chlorine dioxide content dropped from about 88% to 0% (12% to 100% Cl₂). A number of experiments were also carried out in which air was substituted for the nitrogen used in flushing out the reaction vessel. This change had little effect on the yield of perchlorate or the composition of the reactor vapors as compared with identical experiments carried out with nitrogen flushing. These results are given in Tables VII and VIII.

One advantage in using 83% sulfuric acid for carrying out the disproportionation reaction is that less unreacted sodium chlorate and oxidized chlorine gases remain in the reaction mixture. The presence of an appreciable amount of unreacted sodium chlorate could cause difficulties in the separations for the recovery of perchlorate as discussed in Part 4 of the Laboratory Study section of this report. At the end of an average reaction period of 4.5 hours, approximately 3% sodium chlorate and oxidized chlorine gases remain. In contrast, with 70% sulfuric acid, approximately 12% sodium chlorate and oxidized chlorine gases remain after 4.5 hours. This is somewhat counter-balanced by the possibility of the reaction with 83% sulfuric becoming violent in case the reaction temperature is not closely controlled.

It has been established in a few experiments that perchlorates may be made by heating sodium chlorate with perchloric acid. When reacting 60.3% perchloric acid with concentrated (650 g./l.) sodium chlorate solution, the mixture must be heated to 93°C. to obtain an appreciable conversion (16%) of the sodium chlorate to perchlorate. With 70.7% perchloric acid, 32% of the sodium chlorate can be converted to perchlorate at 69°C. The reactor vapors in this case were found to be 98% chlorine dioxide. Raising the reaction temperature with 70.7% perchloric acid to 93°C. did not increase the yield of perchlorate. These results are detailed in Tables IX and X. In the above reactions, the initial HClO₄/NaClO₃ weight ratio with 60.3% perchloric acid was 3.5 and with 70.7% acid it was 4.5. The batch charge in each case was 94.2 mls. of perchloric acid of the given strength and 38.5 mls. of a 650 g./l. NaClO₃ solution (25 gms. NaClO₃).

TABLE VII

Comparison of Yields of Sodium Perchlorate from $\text{NaClO}_3\text{-H}_2\text{SO}_4$ Reaction Under Varied Heating Cycles

(Pot Reactor)

Heating Cycle:

1. Add NaClO_3 solution to cold H_2SO_4 , then heat mixture to desired reaction temperature. Consider reaction period to include heating up time.
2. Add NaClO_3 solution to H_2SO_4 already preheated to reaction temperature.

Gas Used in Flushing Reactor Train	Strength of H_2SO_4 Used- Wt. %	Heating Cycle	Wt. or Mol % of NaClO_3 Converted to NaClO_4
NITROGEN	70	1	32.1
		2	30.0
	83	1	29.5
		2	18.0 *
AIR	70	1	28.5
		2	31.4
	83	1	34.3 ^Δ
		2	33.7

Reaction Charge:

90 mls of H_2SO_4 of given strength
38.5 mls of 650 g./l. NaClO_3

Reaction Temperature:

93°C (with 70% H_2SO_4)
69°C (with 83% H_2SO_4)

Length of Digestion period - 3 hours

* Analysis of reactor solution of this experiment is in question.

^ΔRefer to footnote on Table V, Page 12.

TABLE VIII

Comparison of Composition of Reactor Vapors Formed in $\text{NaClO}_3\text{-H}_2\text{SO}_4$ Reaction Under Varied Heating Cycles -

(Pot Reactor)

Heating Cycle:

1. Add NaClO_3 solution to cold H_2SO_4 , then heat mixture to desired reaction temperature. Consider reaction period to include heating up time.
2. Add NaClO_3 solution to H_2SO_4 already preheated to reaction temperature.

Gas Used in Flushing Reactor Train	Strength of H_2SO_4 used Wt. %	Heating Cycle	Total Wt.* of Cl in Absorbing Solution gms.	% of Cl as Cl_2	% of Cl as ClO_2
NITROGEN	70	1	4.17	75.1	24.9
		2	4.55	99.6	0.4
	83	1	5.50	11.8	88.2
		2	5.49	99.8	0.2
AIR	70	1	3.96	77.9	22.1
		2	4.46	99.8	0.2
	83	1	5.16	8.7	91.3
		2	5.50	100.0	0.0

* Weight of Cl per 25 grams of NaClO_3 charge.

Reaction Charge: 90 mls of H_2SO_4 of given strength
38.5 mls of 650 g./l. NaClO_3

Reaction Temperature: 93°C with 70% H_2SO_4
69°C with 83% H_2SO_4

Length of Digestion Period - 3 hours.

In order to obtain a relatively large amount of product solution for perchlorate recovery studies as described in Part 4 of the Laboratory Study section of this report, four repeated batch reactions of 70% sulfuric acid with 650 g/l sodium chlorate solution (50 gms. NaClO_3 per batch) were carried out at 93°-95°C. by the procedure described above. This series of preparations was repeated using 70.7% perchloric acid in place of the sulfuric acid. During these preparations, an attempt was made to absorb the chlorine-chlorine dioxide off-gases in a train of four concentrated (415 g/l) sodium hydroxide solutions rather than in 8% (87 g/l) sodium hydroxide solutions as above. The absorption by the concentrated caustic solutions was not complete. Use of a 200 g/l sodium hydroxide solution in the absorbers resulted in practically complete absorption of the chlorine-chlorine dioxide off-gases in the first three of the train of four absorbers.

TABLE IX

Effect of Perchloric Acid Strength and Reaction Temperature
on Yield of Sodium Perchlorate

(Pot Reactor)

Strength of HClO ₄ Used Wt. %	Expt. No.	Ave. Max. Reaction Temperature °C.	Wt. or Mol % of NaClO ₃ Converted to NaClO ₄
60.3	33	69	0.0
	34	93	16.0
70.7	35	69	32.1
	36	93	25.2

Length of Digestion Period - 4.5 hours

Reaction Charge: 94.2 mls. of HClO₄ of given strength
38.5 mls. of 650 g./l. NaClO₃ solution

TABLE X

Effect of Acid Strength and Reaction Temperature on Composition of
Reactor Vapors Formed in HClO_4 - NaClO_3 Reaction

(Pot Reactor)

Strength of HClO_4 Used Wt. %	Expt. No.	Ave. Max. Reaction Temp. °C.	Total Wt.* of Cl in Absorbing Solutions gms.	% of Cl as Cl_2	% of Cl as ClO_2
60.3	33	69	0.61	None	100
	34	93	3.32	None	100
70.7	35	69	4.31	2.2	97.8
	36	93	5.19	37.3	62.7

* Weight of Cl per 25 grams of NaClO_3 charge

Length of Digestion Period - 4.5 hours.

b. Packed Column Reactor

In an attempt to avoid the danger of handling and heating large hot batches of acid chlorate-perchlorate solutions as would be necessary on a commercial scale, a semi-continuous, packed column type reactor was designed and built for carrying out the disproportionation of sodium chlorate in acid solution. A reactor of this kind would contain only a small hold-up of potentially dangerous hot chlorate and perchlorate solutions. Details of the column and auxiliary equipment are shown in Figure 1.

A typical experiment will illustrate the operation of the packed column reactor. The charge was prepared by mixing 70% sulfuric acid into sodium chlorate solution (650 g./l.). The chlorate solution was kept in an ice water bath to maintain the temperature during mixing at or slightly below 2 °C. The mixed charge was then held in a feed flask above the column with the charging rate controlled by a stopcock in the line. A slight pressure was maintained above the charge solution to overcome back pressure in the column. The column was heated by an externally wound resistance wire, and the temperatures measured by thermocouples fastened against the outside wall of the glass column. Thus, the measured temperatures were not the actual temperatures of the solutions passing through the column, but were only relative, for use in comparing the results of different experiments. However, it is estimated that the actual average temperature of the acid-chlorate solution in the hot zone of the column was about 40°C. below the outside wall temperature at the midpoint of the heated length of the column. During the downward percolation of the acid-chlorate solution through the glass helix packing of the column, a flow of nitrogen gas was maintained up through the column to dilute the chlorine dioxide content of the vapor below the explosive limit. These gases were either vented to the stack or absorbed in a train of two to four sodium hydroxide solutions of 100-200 g/l. A small bleed of nitrogen gas was maintained through the product receiver to sweep out any chlorine dioxide and chlorine carried down in solution. At the conclusion of a run, the column was washed out with two 100 ml. portions of water.

As seen from Table XI, the packed column reactor was operated through the temperature range of 100° to 180°C. At 180°C. there was a considerable boiling of water from the feed solution, and a repeated refluxing of this water between the condenser and heated portions of the column. At temperatures above 140°C., there was a steadily increasing loss of water by the acid-chlorate mixture as it passed through the column. As these product solutions cooled to room temperature, a considerable precipitation of crystals occurred. Therefore, 140°C. was chosen as a suitable operating temperature at which a conversion of sodium chlorate to perchlorate as high as 31% could be secured in a single pass. Charging rates of 4 to 10 mls. per minute (through a 1-7/32" I.D. column) were suitable, with somewhat higher conversions at the lower throughput. In all cases, the proportions of 70% sulfuric acid and sodium chlorate solution (650 g./l.) were the same as those used in the pot reactions previously described, that is an anhydrous $\text{H}_2\text{SO}_4/\text{NaClO}_3$ weight ratio of 4.1. The nitrogen flushing rate in these experiments was two liters per minute.

FIGURE A

**PACED COLUMN REACTOR
FOR
DISPROPORTIONATION OF SODIUM CHLORATE IN
STRONG ACID**

T. V.

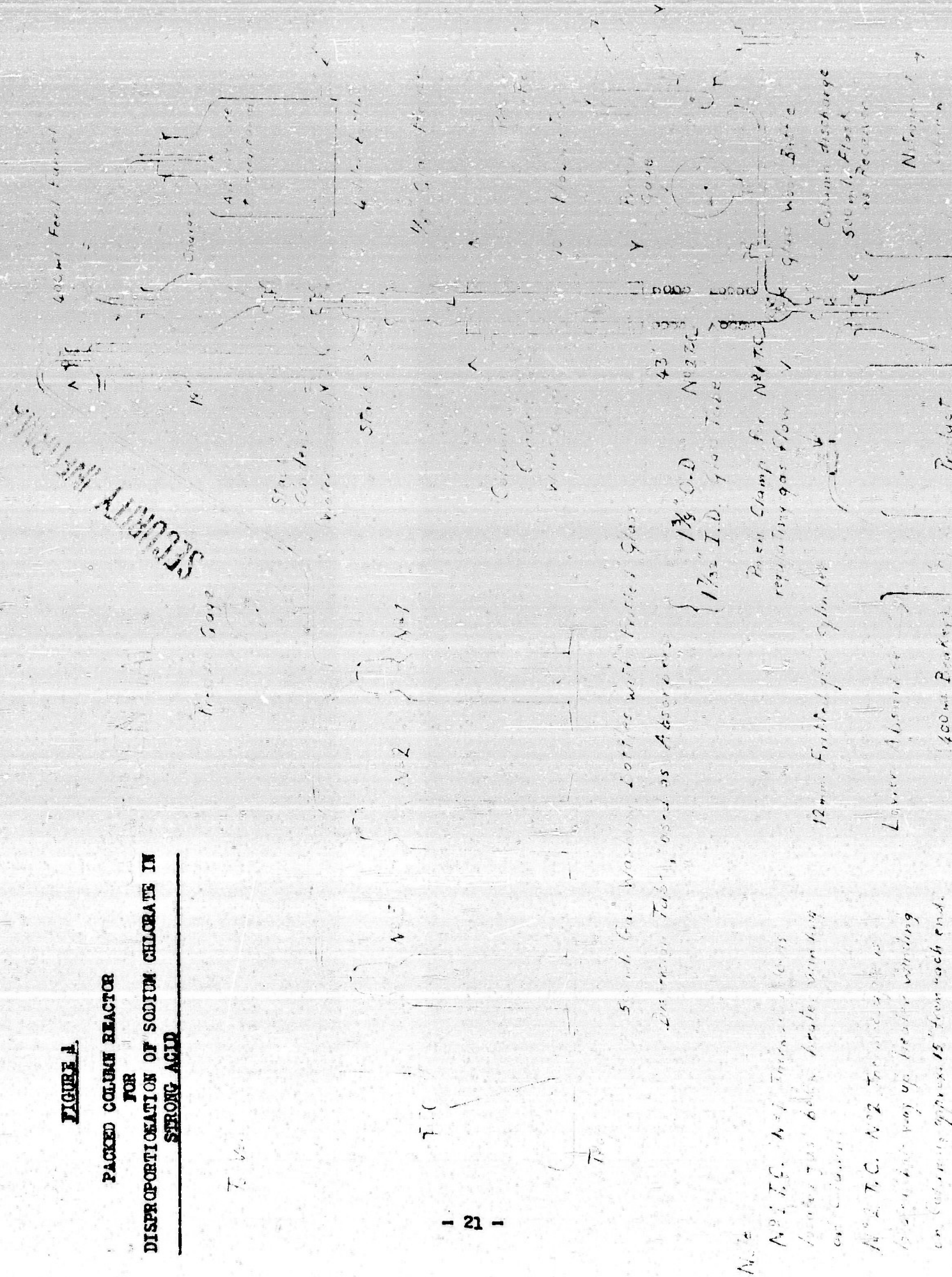


TABLE XI

Yields of Sodium Perchlorate from Packed
Column Reactor

Temperature* on External Wall at Midpoint of Reactor °C.	Charging Rate mls/ min.	Wt. or Mol % Conver- sion of NaClO_3 to NaClO_4
100	2.0	16.8
	4.1	13.0
	8.2	18.0
110	1.46	14.3
	2.24	10.1
	4.35	20.6
	9.3	17.9
120	2.9	13.7
	4.1	16.7
	5.8	17.8
	8.2	16.4
130	4.6	28.4
	7.9	21.2
	8.2 (137°C.)	24.4
140	5.3	31.7
	10.2	27.3
150	5.7	32.3
	8.9	23.3
160	6.6	27.2
	10.2	25.8
170	10.2	21.9
180	9.8	26.7

CHARGE: 60.7 mls. of 660 g./l. NaClO_3 (40g. NaClO_3)
 144 mls. of 70% H_2SO_4
 $[\text{H}_2\text{SO}_4/\text{NaClO}_3$ (anhydrous) weight ratio - 4.1]
 Mixed, then dripped through column.

Nitrogen flushing rate - 2 l./min.

- * - Actual average temperature of acid-chlorate solution in hot zone of column was approx. 40°C. below this outside wall temperature.
- a - Includes NaClO_4 in product solution only.
- b - Includes NaClO_4 in product and wash water solutions.

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The product solutions of several of the above experiments were given a second pass through the column. Nitrogen flushing rates of 2 to 6 liters per minute, and a column temperature of 140°C. were used. At best, only a small increase in conversion of sodium chlorate to perchlorate resulted from the second pass reaction, and at the higher nitrogen flushing rates there was practically no increase in conversion. It thus appears that the minimum nitrogen flushing rate which will lower the chlorine dioxide concentration below the explosive range should be used to permit maximum conversion efficiencies. High flushing rates result in undesirable cooling within the column.

Several experiments were carried out in which perchloric acid was substituted for sulfuric acid in the acid-chlorate charge to the packed column reactor. The proportions of acid to chlorate were those used in the pot reactions (see Table IX and previous discussion). Charges containing 71% perchloric acid crystallized and plugged the reactor at column temperatures above 120°C. (outside wall). A 61% perchloric acid-chlorate charge could be run through the column with column temperatures as high as 150°C. without crystallizing. Considerable difficulty was encountered in analysis of these product solutions, containing high perchlorate, and some refinement of the analytical method is necessary for this type of mixture. Further work with perchloric acid was discontinued because of the more ready interpretation of results when sulfuric acid is used. The data already on hand for perchloric acid from the pot type of reactor, and the patent literature suggests that both acids can be used for the disproportionation.

As previously discussed, it is felt that sulfuric acid and sodium chlorate when reacted under the conditions used in this research form chlorine dioxide as the only chlorine-containing oxidizing gas, and, therefore, a 33.3% conversion of sodium chlorate to perchlorate represents the theoretical maximum yield. As this chlorine dioxide is swept out of solution by the flushing gas (air or nitrogen) it becomes susceptible to thermal decomposition into chlorine and oxygen, the rate of this reaction being quite high above 60°C. Therefore, the off-gases from the chlorate-acid reaction may contain as little as one-fifth of the original oxidizing power of the chlorine dioxide formed by the time they pass over to the caustic solution absorbers.

In a typical experiment with 70% sulfuric acid, approximately 30% of the chlorate charge is converted to perchlorate, 25% to 30% remains in the product solution (and wash solutions, if used in column experiments) as dissolved chlorine dioxide, chlorine, and possibly some unreacted chlorate, and 40% to 45% is recovered as dissolved chlorine dioxide and chlorine in the caustic solution absorbers. As seen from Table VIII the oxidizing level of the caustic absorbed off-gases from the reaction with 70% sulfuric acid at a temperature sufficiently high to obtain a satisfactory perchlorate yield, would be expected to be between 75% to 100% chlorine (25% to 0% ClO₂). These figures refer to reactions carried out in a pot reactor. The composition of the absorbed off-gases from the 70% sulfuric acid-chlorate mixture reaction in the packed column reactor also falls in this range, generally being close to 100% chlorine (0% ClO₂).

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Assuming that a 100% efficient reaction is one in which 66-2/3% of the chlorate is converted to chlorine dioxide, all of which is absorbed in caustic at the full oxidizing level, then in practice, when reacting 70% sulfuric acid with sodium chlorate solution (650 g/l), there is only a 13% to 27% overall efficiency in recovery of oxidizing values in the caustic solution absorbers. Improvements in the process to make possible the complete release of oxidizing gases from the product solution and recovery in the caustic solution absorbers may be expected to increase the efficiency in recovery of oxidizing values to from 21% to 42%.

As seen from Table IV, practically pure chlorine dioxide can be recovered in the caustic absorber solutions by lowering the reaction temperature with 70% sulfuric acid. However, as seen from Table II, the conversion of chlorate to perchlorate is considerably lower, and the reaction takes place very slowly. A multi-stage processing might be considered with relatively low temperatures in the early stage or stages for efficient oxidizing value recovery, and a gradual rise in temperature in the later stage or stages to complete the conversion of the chlorate to perchlorate.

Referring to Tables I and II, one may observe that conversions of sodium chlorate to perchlorate in excess of 30% were obtained with 83% sulfuric acid in a pot reactor with the oxidizing level of the absorbed off-gases maintained at 85-88% chlorine dioxide. Therefore, it seemed that the recovery of oxidizing values in the absorbed off-gases from the packed column reactor could be most easily and sharply increased by substituting 83% sulfuric acid for the 70% sulfuric acid. However, the substitution of an equal volume of 83% sulfuric acid for the 70% acid resulted in the formation of a heavy crystalline precipitate on mixing with the sodium chlorate solution, with the mixture maintained at or slightly below 25°C. Such a slurry would not have been suitable for use as a charge to the packed column reactor.

On mixing 83% sulfuric acid with 650 g/l sodium chlorate solution in various proportions through the $H_2SO_4/NaClO_3$ weight ratio range of 0.5 to 8.9, a crystalline precipitate was formed in every case. The mixture was more strongly yellow when the chlorate was added to the acid than vice versa. The filtered precipitate from the reaction carried out at the $H_2SO_4/NaClO_3$ weight ratio of 6.8 at 30°C. was found to contain 0.4% sodium chlorate and no sodium perchlorate. This corresponded to an 0.8% loss of the sodium chlorate charge. The precipitate was composed of sodium bisulfate, sulfuric acid and water, which was mostly held as water of hydration. The choice of an $H_2SO_4/NaClO_3$ weight ratio of 6.8 used in the following experiments with 83% sulfuric acid was made on the basis of completeness of precipitation of sodium ion on mixing acid and chlorate, general observations on carrying out the precipitation reaction, and greater safety in diluting the chlorate with a relatively large amount of sulfuric acid.

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In view of the small loss of chlorine compounds in the bisulfate-acid precipitate, it was proposed to carry out the reaction of 83% sulfuric acid and sodium chlorate solution (650 g./l.) in two steps. First, the acid and chlorate solutions would be mixed, with the temperature maintained near that of room. Then, the precipitate would be filtered off, and the filtrate passed through the heated packed column reactor in the same manner as described above for a 70% sulfuric acid-sodium chlorate solution mixture. Tables XII and XIII show in detail the data and calculated results for three typical experiments on the disproportionation of sodium chlorate with 83% sulfuric acid in a packed column reactor by the above procedure. Satisfactory conversions (29-30%) of sodium chlorate to perchlorate were obtained, and the absorbed off-gases contained 79 to 89% chlorine dioxide, demonstrating a high level of recovery of oxidizing values. The $H_2SO_4/NaClO_3$ weight ratio in the above experiments was 6.8.

Based on laboratory experience with the above two stage process, the following detailed procedure is recommended for laboratory scale preparations handling up to one pound of sodium chlorate:

Add the sodium chlorate solution (650 g./l.) at the rate of about 4 to 6 ml./min. to the 83% sulfuric acid contained in a closed vessel. Maintain the reactor temperature at 35°-40°C., and continuously flush the reactor vapor space with air or nitrogen at 1 to 2 l./min. Pass the reactor gases through a train of at least three absorbers, each containing 250 ml. of 100-200 g./l. sodium hydroxide to remove all oxidizing values, and having a sintered glass gas washing inlet tube. Keep the caustic absorbers cooled in a water bath to 20°-25°C. An approaching saturation or neutral point of a given absorber solution at the head of the absorption train is indicated by the appearance of successively darker shades of amber color in the solution. When the solution has reached a moderate but not dark amber color, remove the absorber from the line, and simultaneously add a fresh absorber at the end of the train of absorbers. Check the pH of the saturated absorber solution and add concentrated sodium hydroxide solution or pellets to maintain pH 8 or higher.

A more uniform reaction is promoted by keeping the reactor slurry constantly agitated by a low speed paddle type stirrer. After all the sodium chlorate solution has been added, allow the reactor temperature to drop slowly to that of room, but maintain the air or nitrogen flushing and stirring for one to two hours to sweep out dissolved oxidizing gases. Chill the mixture slowly and with stirring to 15°-20°C., and vacuum filter while cold through a sintered glass filter funnel. Maintain a bleed of air or nitrogen through the filter flask to sweep out oxidizing gases through the same train of caustic solution absorbers as was used in the above mixing operation.

Filter the $NaHSO_4-H_2SO_4$ cake as dry as possible; remove from the filter, and place in a vacuum desiccator for further drying. The filtrate is then passed down through the packed column reactor, following the procedure described in Section 2b and Figure 1 of this

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TABLE XII

DISPROPORTIONATION OF NaClO_3 WITH 8% H_2SO_4 IN PACKED COLUMN REACTOR - DATA

EXPERIMENT NO.	COLUMN CHARGE			CHARGING RATE ML/S. MIN.	AVE. TEMP. ON EXTERNAL WALL AT MIDPOINT OF REACTOR-°C.	N ₂ FLUSH RATE L/MIN	WT. OR MOL. % CONVERSION OF NaClO_3 TO NaClO_4	% RECOVERY OF NaClO_3 CHARGE	OXIDIZING LEVEL OF ABSORBER SOLNS. 100% ClO_2 (LESS NaClO_4)	TOTAL CHLORINE CMFDS. REC'D IN ABSORBER SOLNS. AS % OF CHARGE (LESS NaClO_4)	COMPOSITION OF ABSORBED OFF-GASES EXPRESSED AS:	
	MLS. OF NaClO_3 SOLN. 650g/l	MLS. OF 8% H_2SO_4	TOTAL MIXED VOL. MLS. GMS.								WT. % Cl_2	WT. % ClO_2
108	75	225	300 280 (Filtrate) 64.1g.-ppt	6.7	110.5	0.5	30.2	95.5	85.0	60.0	10.9	89.1
109 (1st Pass)	75	225	300 277 (Filtrate) 53.1g.-ppt	5.0	110.5	0.5						
109 (2nd Pass)			270	5.1	150	0.5	29.1	92.9	79.3	63.1	15.7	84.3
110 (1st Pass)	75	225	300 275 (Filtrate) 53.0g.-ppt	5.5	115	0.5						
110 (2nd Pass)			270	5.4	159.5	0.5	29.8	93.7	72.5	62.2	21.2	78.8

(*) Actual temperature of acid-chlorate solution within column was approximately 40°C. below this outside wall temp.

GENERAL NOTES:

- (1) Nitrogen flushing gas was saturated with H_2O at 50°C., and heated to 100°C. before introduction into the bottom of the column.
- (2) Weight ratio of $\text{H}_2\text{SO}_4/\text{NaClO}_3=6.8$.

TABLE XIII

DISPROPORTIONATION OF NaClO_3 WITH 83% H_2SO_4 IN PACKED COLUMN REACTOR -
ANALYTICAL RESULTS
83% H_2SO_4

83% H₂SO₄

EXPERIMENT NO.	PRODUCT ANALYSIS		WASH		ABSORBER SOLUTION ANALYSIS					ANALYSIS OF NaHSO ₄ -H ₂ SO ₄ ppt. FORMED UPON MIXING NaClO ₃ SOLUTION AND ACID
	NaClO ₃	NaClO ₄	SOLN. ANALYSIS		NaCl	NaClO	NaClO ₂	NaClO ₃	NaClO ₄	
			NaClO ₃	NaClO ₄						
		← GRAMS →		← GRAMS →						
108	1.63	14.7	1) 0.55 2) 0.04	1.75 0.22	1) 1.90 2) 0	1.35 0	8.83 0.76	11.68 0.83	0.26 TR	0.40 g. NaClO ₃ (0.82% of Charge) 0 g. NaClO ₄
109 (1st Pass) 109 (2nd Pass) 0.29	- 16.2	- 16.2	1) LOST 2) 0.03	LOST 0.08	1) 3.67 2) 0	0.58 0	7.33 0.70	12.95 0.83	- 0 0	0 g. NaClO ₃ 0 g. NaClO ₄
110 (1st Pass) 110 (2nd Pass) 0.32	- 16.23	- 16.23	1) 0.05 2) TR	0.18 TR	1) 4.29 2) 0	1.25 0	7.15 0.48	11.17 0.58	0.21 0.08	0.40 g. NaClO ₃ (0.82% of Charge) 0 g. NaClO ₄

report. A charging rate of 5-6 ml./min. and an air or nitrogen flushing rate of 0.5-1.0 l./min. has been found suitable. Saturate the air or nitrogen with H_2O at $50^\circ C$. and heat to $100^\circ C$. before introduction into the bottom of the column. Pass the column off-gases through the same train of caustic solution absorbers as was used in the above two operations.

A 30% conversion of sodium chlorate to perchlorate may be obtained by a single pass of the filtrate through the column at an average external wall column temperature of $110^\circ C$. The slight yellow color in this product may be removed by a second pass through the column at an external wall temperature of about 140° - $150^\circ C$.

The recovery of perchlorate from the product solution is described in Part 4 of the Laboratory Study Section of this report, and the recovery of oxidized chlorine values from the absorber solutions in Part 5.

3. Effect of Catalysts on the Acid Disproportionation of Sodium Chlorate in a Pot-Type Reactor

The purpose of this phase of the work was to determine if the acid disproportionation of sodium chlorate could be catalyzed to give higher conversion of sodium chlorate to sodium perchlorate and also to see if the oxidizing level of the gases swept out of the reaction solution could be changed.

This study was carried out in a pot type reactor (a 250 ml. gas washing bottle) containing 70% sulfuric acid and the catalyst. Sodium chlorate solution was introduced from a burette into the reactor. A stream of nitrogen swept the yellow gases from the reactor through two 250 ml. gas washing bottles containing sodium hydroxide solution. See Figure 2 for diagram of apparatus.

To carry out the acid disproportionation of sodium chlorate, 90 ml. of 70% sulfuric acid was placed in the reactor together with the catalyst (10% by weight of the sodium chlorate used on a solid basis). Then 38.5 ml. of sodium chlorate solution (650 g./l.) was slowly added at a rate from 0.8 to 1.4 ml./min. with continuous nitrogen flushing through the reactor and sodium hydroxide scrubbing solutions (200 g./l. NaOH, first scrubber; 100 g./l. NaOH, second scrubber), at about $1/3$ l./min. After all of the sodium chlorate solution had been added, the temperature of the reactor was slowly raised to between 90° to $95^\circ C$ over a 1.5 to 1.75 hour period. The reaction temperature (90° - 95°) was maintained for about 3 hours. Nitrogen was flushed through the system continuously to prevent the build-up of high concentrations of chlorine dioxide in the reactor. At the end of the 3 hour period the apparatus was dismantled, nitrogen flush stopped and the reactor solution allowed to cool. The solid catalyst remaining was filtered from the reactor solution and the solution analyzed. The caustic scrubber solutions were also analyzed. Results are shown in Tables XIV and XV.

Figure 2
Acid Disproportionation of Sodium Chlorate in a pot-type Reactor using Catalysts.

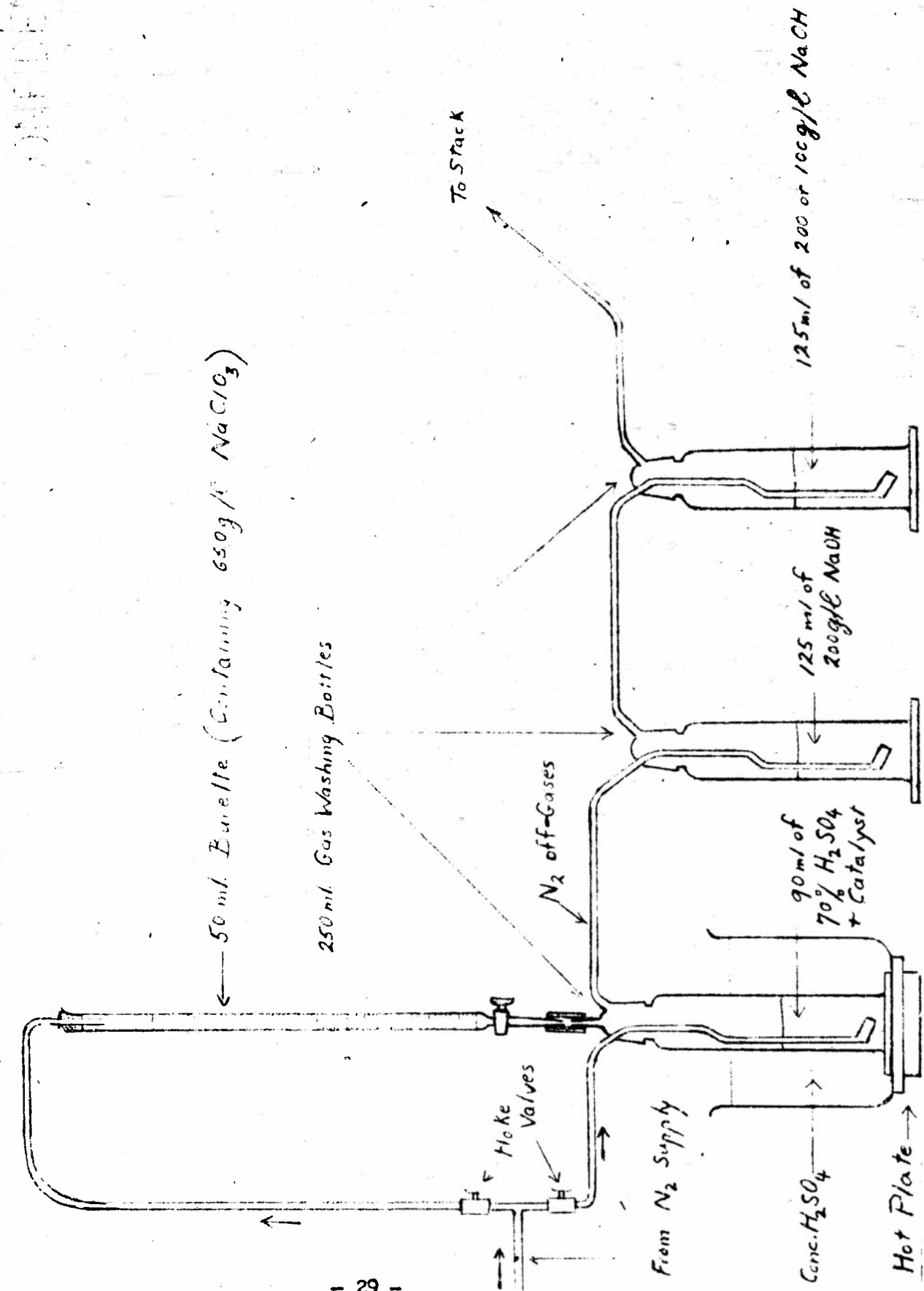


TABLE IV
SECURITY INFORMATION
ACID DISPROPORTIONATION OF SODIUM CHLORATE IN A POT-TYPE REACTOR USING CATALYSTS-DATA

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CATA- LYST	WGT. OF CATA- LYST	CHARGE		CHARGING RATE OF NaClO ₃ CORT. SOLN. ml/min.	N ₂ FLOW RATE l/min.	TIME FOR REACTOR TO REACH 92°C. HOURS	AVERAGE REACTOR TEMP. °C.	TIME IN HOURS AT REACTION TEMP.	WT. OR MOL % CONVER- SION OF NaClO ₃ to NaClO ₄	% RECOV- ERY OF NaClO ₃ CHARGE	CLIDIC- ING LEVEL OF ABSOR- BER SOLN 100% = ClO ₂ (less NaClO ₄)	TOTAL CHLORINE COVDS. RE- COVERED 15 ABS. SOLNS. AS % OF RE- ACTOR	NOTES
		MLS. OF NaClO ₃ -70% SOLN. H ₂ SO ₄ 650 g/l	SOLID NaClO ₃ CORT. SOLN. GRAMS										
None	0	38.5	90	0.82	0.33	1.5	92	2	28.8	100	98.3	58.1	One small explosion pushed reactor lid off.
PbO ₂ (2)	2.8	38.5	90	1.28	0.33	0.32	100	3	32.3	98.5	25.6	59.0	
PbO ₂ (2)	2.8	38.5	90	0.77	0.33	4.0	94	2.33	31.1	97.8	94.4	54.1	Cap of reactor lid popped off for an unknown length of time, thus lowering recovery in absorber soln Burette plugged during addition of NaClO ₃ soln.
MnO ₂	2.8	38.5	90	1.1	0.33	1.33	95	3	29.2	50.5	73.0	23.4	
Fe ₂ O ₃	2.8	38.5	90	0.77	0.33	1.1	94	3	22.8	94.0	98.4	56.2	Slight amount of off-gases out and absorber.
CuSO ₄	2.8	38.5	90	1.28	0.33	1.75	94	3	27.1	89.5	96.3	57.7	
FeSO ₄	2.8	38.5	90	1.38	0.33	1.33	94.5	3	26.4	70.3	21.5	55.0	Bubb back in Tygon tubing during S ₂ cylinder change.
MnSO ₄	2.8	38.5	90	1.42	0.33	1.45	92.8	3	26.5	87.5	97.2	49.8	
MnSO ₄	2.8	38.5	90	0.92	0.33	1.57	93	3	17.0	51.8	74.1	55.8	
FeO	2.8	38.5	90	1.6	0.33	1.33	93.8	3.17	9.37	81.5	63.0	53.4	

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TABLE XI

ACID DISPROPORTIONATION OF SODIUM CHLORATE IN A POT TYPE REACTOR USING CATALYSTS
ANALYSIS OF SOLUTIONS

CATALYST	PRODUCT SOLUTION ANALYSIS					FIRST ABSORBER SOLN. ANALYSIS					SECOND ABSORBER SOLN. ANALYSIS				
	NaCl	NaClO	NaClO ₂	NaClO ₃	NaClO ₄	NaCl	NaClO	NaClO ₂	NaClO ₃	NaClO ₄	NaCl	NaClO	NaClO ₂	NaClO ₃	
	← TOTAL GRAMS →					← TOTAL GRAMS →					← TOTAL GRAMS →				
None	-	-	-	3.3	8.3	0.17	0	5.6	6.8	0	0	0	0.37	0.4	
PbO ₂ (1)	-	-	-	1.8	9.3	4.1	4.1	0.24	0.95	0	0	0	0.13	0.04	
PbO ₂ (2)	0.11	TR	0.09	2.9	8.95	0.56	0.10	4.4	5.8	0	0	0	0.58	0.70	
K ₂ O ₂	-	-	0	2.0	8.4	0.66	0.51	1.46	2.1	0	0	0	0.06	0.03	
Fe ₂ O ₃	-	-	-	1.3	6.55	0.17	0	4.8	6.0	0	0	0	0.9	1.0	
Cu ₂ O ₄	-	-	-	1.2	7.8	0.31	0.09	4.8	6.1	0	0	0	0.84	1.0	
FeSO ₄	-	-	-	1.24	7.6	0.68	0	4.9	6.6	0	0.10	0	0.4	0.5	
H ₂ SO ₄	-	-	-	1.5	7.65	0.23	0	4.91	6.13	0	0	0	0.6	0.7	
MnSO ₄	-	-	-	1.4	4.6	0.6	0	5.25	7.05	0	0	0	0.3	0.4	
FeO·Fe ₂ O ₃	-	-	0.09	4.1	2.7	2.5	1.1	2.0	4.2	0	0	0	0.48	0.63	

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Of the catalysts tried, namely: lead dioxide, manganese dioxide, ferric oxide, magnetite, copper sulfate, ferrous sulfate, nickel sulfate and manganous sulfate, none appreciably increased the conversion of sodium chlorate to sodium perchlorate or changed the oxidizing level of the absorber solutions from that obtained without the use of catalyst. In fact, manganous sulfate and magnetite actually gave lower conversions of chlorate to perchlorate.

4. Recovery of Perchlorate

The following methods of recovering perchlorate from solutions resulting from the disproportionation of chlorate in strong acid solution were considered:

- (1) Fractional crystallization of sodium perchlorate.
- (2) Addition of anhydrous HCl to precipitate sodium ion as sodium chloride, filtering, and heating to drive off excess HCl. Pure perchloric acid should remain when it is used as the strong acid in the disproportionation of chlorate.
- (3) Same as (2) except vacuum distillation will be necessary to separate perchloric acid from the concentrated sulfuric acid when sulfuric acid is used as the strong acid in the disproportionation of chlorate.
- (4) Vacuum distillation of perchloric acid from solutions resulting from the disproportionation of chlorate in strong sulfuric acid. Even if this is possible, sodium will remain behind in the still residue as sodium acid sulfate. This salt may be removed by cooling the still residue, but some acid values would then be lost.
- (5) Precipitation of potassium perchlorate or ammonium perchlorate by the addition of potassium sulfate or ammonium sulfate.

Method (1) (Fractional crystallization of sodium perchlorate) was shown to be impractical with sulfuric acid-sodium chlorate product solutions, since solubility studies indicated that sodium perchlorate was too soluble at 0°C. in sulfuric acid solutions to be crystallized out of solutions of the low perchlorate concentration resulting from the disproportionation of chlorate in concentrated sulfuric acid solution. Perchloric acid-sodium chlorate product solutions showed more promise with this method. A liter of disproportionation product was formed using 71% perchloric acid instead of sulfuric acid. Sodium perchlorate was precipitated by chilling the product solution. At 2°C., the sodium perchlorate crystal crop was 1.4 times the reaction yield from sodium chlorate. It thus seems desirable to control the crystallization temperature so as to remove only the sodium perchlorate formed in the disproportionation reaction and to remove the excess sodium ion as sodium chloride by adding anhydrous HCl. All the carrier perchloric acid may then be recycled after suitable re-concentration. Alternatively, all the sodium ion may be precipitated and product perchloric acid separated. The perchloric acid would have to be distilled should a higher concentration than the product solution (approx. 60% HClO₄) be desired.

Method (2) (Addition of anhydrous HCl) was not thoroughly studied. However, preliminary experiments indicated that about 70% of the sodium ion remaining in the filtrates from the ammonium and potassium perchlorate precipitations may be precipitated as sodium chloride from the sulfuric acid solution by saturating it with anhydrous HCl.

Method (3) was not experimentally studied.

Method (4) (Vacuum distillation of perchloric acid) has been shown to be practical. By working with a synthetic reactor solution of the following composition:

$\text{NaClO}_4 \cdot \text{H}_2\text{O}$	-	90.2 grams
Na_2SO_4	-	91.0 grams
$\text{H}_2\text{SO}_4 (95.5\%)$	-	435 mls.
H_2O	-	572 mls.
Total Volume - 1000 mls.		

it was found that 95% of the perchlorate could be recovered as perchloric acid by vacuum distillation. In a typical run 250 ml. of the synthetic reactor solution was charged into a standard distillation apparatus. To prevent bumping and the formation of solid hydrates of perchloric acid steam was slowly bled into the boiler through a capillary tube. At a vacuum of between 27 and 27-1/2 inches the first condensate of water was observed between 41°C. and 45°C. vapor temperature. This water cut was removed from the liquid receiver and the still temperature slowly raised. At a pot temperature of 128°C. and a vapor temperature of 92°C., perchloric acid started to distill over and was complete when the pot reached 196°C. and a vapor temperature of 116°C. This cut of 36.5 gm. was found to be 41.6% perchloric acid and 2.9% sulfuric acid. The residue of 206.5 gm. was found to be 95.1% sulfuric acid (based on $\text{SO}_4 =$ content) with 2% perchloric acid.

Method (5) (Precipitation of perchlorates) is the favored method for recovery of potassium perchlorate from product solutions. More research effort was expended on developing this method than on the other methods.

In the first procedure used, about 84% of the perchlorate present in the disproportionation reactor solution was recovered as ammonium and potassium perchlorate. 43% of the perchlorate was recovered as the ammonium salt and 41% as potassium perchlorate. Ammonium and potassium chlorides were used as the precipitating salts. In the second procedure tested, the use of sulfates instead of chlorides of ammonium and potassium resulted in elimination of foaming during the reaction, and 85% of the product solution perchlorate was recovered. In the above two procedures, 100% excesses of ammonium and potassium salts were used. The presence of the excess ammonium and potassium ion in the solution after precipitation of the product perchlorate would be undesirable on a commercial scale, since this depleted product solution would be recycled for its acid content.

The following procedure was developed in which the overall excess of ammonium and potassium salts was 20%, the amount of wash water was decreased and slurrying was eliminated. By this procedure, 81.2% of the product solution perchlorate was recovered as ammonium (49.3%) and potassium (31.9%) perchlorates. These perchlorates contained some sulfate which would have to be removed by a recrystallization.

Modification #3

For every mol of sodium perchlorate in the product solution, slowly add 0.4 mol ammonium sulfate as the dry salt to the product solution maintained at 50°C. When all solids have been dissolved, cool to 2°C., and vacuum filter while cold through a sintered glass funnel. Wash the precipitate with ice water, using 1/100th of the original solution volume, first breaking the vacuum before adding the wash water. Filter quickly and vacuum dry the precipitate in a desiccator containing anhydrous calcium sulfate.

To the above combined filtrate heated to 50°C., slowly add 0.2 mol of potassium sulfate for each mol of sodium perchlorate present in the original product solution. When all solids have been dissolved, cool to 2°C., and vacuum filter while cold through a sintered glass funnel. Wash the precipitate with ice water using 1/150 of the original solution volume, first breaking the vacuum before adding the wash water. Filter quickly and vacuum dry in a desiccator containing anhydrous calcium sulfate.

In the following procedure, all of the perchlorate in the product solution was recovered in one precipitation as the potassium salt, and only 10% excess potassium sulfate was used. By this simplified procedure, 88.5% of the product solution perchlorate was recovered as potassium perchlorate. This potassium perchlorate contained some sulfate which would have to be removed by a recrystallization.

Modification #4

For every mol of sodium perchlorate in the product solution, slowly add 0.55 mol potassium sulfate as the dry salt to the product solution maintained at 50°C. When all solids have been dissolved, cool to 2°C., and vacuum filter through a sintered glass funnel. Slurry the precipitate with ice water using 1/80th of the original solution volume. Filter quickly and vacuum dry the precipitate in desiccator containing anhydrous calcium sulfate.

88.2% of the product solution perchlorate was recovered as potassium perchlorate by a Modification #5 recovery method similar to Modification #4 above, except that only 4% excess potassium sulfate was used, and the wash water used was 1/50th of the original solution volume and was added at room temperature, the mixture then being cooled to 2°C. for filtering. By recovery

method Modification #6 which was similar to #5, except that the product precipitate was water slurried twice, 85.7% of the product solution perchlorate was recovered as potassium perchlorate. The extra water slurrying with Modification #6 reduced the sulfate content of the product to less than one-half that obtained with #5.

5. Recovery of Oxidized Chlorine Values

The volatile off-gases resulting from the disproportionation of sodium chlorate in concentrated sulfuric acid were absorbed in aqueous sodium hydroxide (100 g./l. or 200 g./l.). These gases consisted mainly of chlorine dioxide, chlorine and oxygen with some perchlorate mist, and when absorbed in aqueous sodium hydroxide, were converted into sodium chloride, sodium hypochlorite, sodium chlorite, sodium chlorate and sodium perchlorate. The compositions of such absorber solutions resulting from the acid disproportionation of sodium chlorate are discussed in detail under part 2a of the Laboratory Study section of this report, and were found to vary somewhat from run to run depending upon reaction conditions.

To convert these degraded chlorine compounds to sodium chlorate, which could then be recycled to the acid disproportionation column, several methods were considered:

1. Electrolysis in a sodium chloride-sodium chlorate type cell
2. Addition of more sodium hypochlorite and adjustment of pH to between 6 and 9, to favor the reaction:
$$\text{NaClO}_2 + \text{NaClO} \longrightarrow \text{NaClO}_3 + \text{NaCl}$$
3. Catalytic disproportionation of sodium chlorite to sodium chlorate and sodium chloride.

As the electrolytic method using existing plant equipment appeared to be the most promising, the main effort was directed toward the electrolytic conversion of these absorber solutions to sodium chlorate, while only preliminary work was done on the last two methods.

a. Electrolysis of Absorber Solutions in a Sodium Chloride-Sodium Chlorate Type Cell

Work with Synthetic Solutions

At this time quantitative analytical methods had not as yet been developed to determine the amount of sodium chlorite remaining in electrolyzed sodium chlorite solutions. So it was decided to electrolyze synthetic absorber solutions with definite NaClO_2 make-up, and obtain X-ray analysis of the solid electrolyzed products.

Four preliminary runs were made using graphite and platinum iridium (10%) anodes and electrolyzing synthetic absorber solutions consisting of aqueous sodium chlorite and sodium chlorite-sodium chloride mixtures at 2°-5°C. In these experiments, no attempt was made to control pH and no mechanical agitation of the electrolyte was used. The calculated current efficiency varied from 30 to 90% but nevertheless sodium chlorate was formed, and no large amount of sodium chlorite remained as shown by X-ray analysis (chemical analytical methods, then used, would not distinguish between sodium chlorite and sodium chlorate). These results are shown in Table XVI. In the electrolysis using platinum-iridium anodes, a dark brown layer formed in the electrolyte which at first was assumed to be unstable, explosive higher oxides of chlorine, but after continued electrolysis the entire electrolyte became water white.

After it became clear that these cells were not dangerous, it was decided to control the pH of the electrolyte manually by the addition of 37-38 weight percent hydrochloric acid. To obtain uniform composition of the electrolyte, the cell was equipped with a mechanical stirrer. According to the results shown in Table XVII, electrolysis in slightly alkaline electrolyte at 0° to 8°C., gave a somewhat lower current efficiency (from 52 to 63%) than slightly acid electrolyte (from 63 to 79%), using graphite anodes. Although sodium dichromate is used in commercial chlorate cells, the addition of 4 g./l. of sodium dichromate to the sodium chlorite-sodium chloride electrolyte apparently did not increase the current efficiency. Chemical analytical methods were developed to determine sodium chlorite as such and none was detected.

The erosion rate of a new graphite anode increased from 2 lbs. to 25 lbs. of anode eroded per ton of chlorate formed after four runs. When a magnetite anode was used under similar conditions, the erosion rate was found to be about 7 lbs. of anode eroded per ton of chlorate formed.

Work with Absorber Solutions

Three absorber solutions in which the caustic content had been neutralized by the absorption of off-gases from the acid disproportionation of one (1) lb. of sodium chlorate were combined, fortified with more sodium chloride and sodium dichromate added (4 g./l. of $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$). After electrolysis in a chlorate-type cell with a graphite anode, the resulting electrolyte analyzed about 400 g./l. of sodium chlorate and about 111 g./l. of NaCl with only a trace of NaClO_2 found. The current efficiency was about 63% with about 93% recovery of the solid material after electrolysis. On electrolysis of a similar absorber solution from another disproportionation experiment, the electrolyte analyzed 450 g./l. of sodium chlorate, 88 g./l. of NaCl, and 16.7 g./l. NaClO_2 . The current efficiency was about 72% with about 89% recovery of the solid material after electrolysis. Details of these electrolyses are

TABLE XVI
ELECTROLYSIS OF SYNTHETIC ABSORBER SOLUTIONS - PRELIMINARY

CONDITIONS:

Anode Current Density: 69 amperes/sq.ft.
No mechanical agitation
pH not controlled by addition of conc. HCl to electrolyte
Temp. of Electrolyte - 2°-5°C.

Anode Material	Electrolyte		X-Ray Analysis of Solid Product	Wts. of Products According to Chemical Analysis - Grams			Paradays to Form Product	Paradays According to Current and Time	Current Efficiency %
	NaClO ₂ g./l.	NaCl g./l.		NaCl	NaClO ₃	NaClO ₄			
Graphite	424	none	NaClO ₃ + Some NaCl	23.8	133.3	None	2.5	3.59	70
Platinum-Iridium	424	none	NaClO ₃ + Some NaCl	25.7	87.8	2.64	1.74	1.87	93
Platinum-Iridium	350	40	NaClO ₃ + Some NaCl	30.1	75	2.72	1.48	3.36	44
Platinum-Iridium	282	91.5	--	29.1	80.8	None	1.52	5.72	27

TABLE XVII
ELECTROLYSIS OF SYNTHETIC ABSORBER SOLUTIONS - EXTENDED RUNS

CONDITIONS: Anode Current Density - 0.5 amperes/sq. cm.
Mechanical agitation

pH controlled by addition of 30% HCl to electrolyte

Temp. of electrolyte - 60-65°C.

Stainless steel-(304) Cathodes

Anode Material	Electrolyte			Vol. of 30% HCl added to cont. pH at	Vol. of X-Ray Analysis of Solid Product	Wts. of Products According to Chemical Analysis - Grams				Paradays to Form Product	Paradays According to Current Efficiency and Time	Current Efficiency %	Lbs. of Anode Eroded Per Ton of Chlorate Formed
	NaClO ₂ g/l	NaCl g/l	NaCr ₂ O ₇ 2H ₂ O g/l			NaCl	NaClO	NaClO ₂	NaClO ₃	NaClO ₄			
Graphite	282	91.5	-	9-11	NaClO ₃ +	30.76	Not Analyzed	None	155	None	4.14	6.54	63
Graphite	282	91.5	-	6-7	-	33.76	Not Analyzed	None	148	21	5.04	6.42	79
Graphite	282	92	4	8-9	NaClO ₃ +	17	None	None	179	Not Analyzed	5.28	10.0	52.8
Graphite	282	92	4	7-8	NaClO ₃ +	16	None	None	185	Not Analyzed	5.4	10.3	52.4
Magnetite	282	92	-	8-9	NaClO ₃ +	32	None	None	99	Trace	2.08	3.96	52.5
Graphite	282	91.5	-	8-9	NaClO ₃ +	44	None	None	161	Not Analyzed	3.34	7.05	55.9
Graphite	282	91.5	-	6-7	NaClO ₃ +	42	1	None	155	Not Analyzed	4.37	5.35	91.7
Graphite	282	91.5	4	6-7	NaClO ₃ +	22	None	None	200	None	6.39	9.06	63.2
Graphite	282	91.5	4	3-9	NaClO ₃ +	43	None	None	164	Not Analyzed	3.48	5.55	52

New Graphite Anode

1.92

5.3

2.6

25

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TABLE XVIII
ELECTROLYSIS OF COMBINED ABSORBER SOLUTIONS

CONDITIONS: Graphite anode
Anode current density - 69 amperes/sq.ft.
Temperature of Electrolyte - 4-5°C.
4 g./l. $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ Added

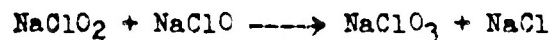
Exp. No.	Electrolyte				pH Cont. at	Volume of 38% HCl Added to Control pH ml.	Wts. of Products According to Chemical Analysis - Grams			Faradays to Form Product	Faradays According to Current	Current Efficiency cy %	Recovery of Chlorine Compds. %	
	Combined Absorber Soln		NaCl Added to Comb. Abs. Soln. Grams	Volume After Adding NaCl ml.			NaCl	NaClO ₂	NaClO ₃					
	Total Grams													
	NaCl	NaClO ₂	NaClO ₃											
111	15.3	65.6	109	219	990	6-7	32	111	Trace	400	13.79	21.8	63.2	92.5
113	9.9	70.2	112.5	234.2	1000	6-8	51	88	18	450	16.74	23.4	71.6	89

shown in Table XVIII. The disproportionation experiments from which the above absorber solutions were obtained are described in Tables XIX and XX and part 6 of the Laboratory Study section of this report.

b. Addition of More Sodium Hypochlorite and Adjustment of pH

Some preliminary work was done on the reaction between sodium chlorite and sodium hypochlorite to form sodium chlorate and sodium chloride.

J. F. White, M.C. Taylor and G.P. Vincent (3) found that the reactions of a solution containing both a chlorite and hypochlorite depend upon its pH. In very alkaline solutions, mixtures of chlorite and hypochlorite ions undergo little reaction in a period of hours. At low alkalinity (pH from 6 to 9), where hypochlorous acid is also present, a chlorate and chloride are rapidly formed, sometimes accompanied by a trace of chlorine dioxide. The overall reaction is:-

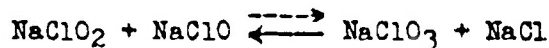


However, in all acid solutions, (pH from 2 to 6) chlorine or a hypochlorite causes the chlorite to disappear immediately upon mixing, chlorine dioxide being formed.

Thus it was thought that if the direct electrolysis of absorber solutions containing chlorite was unsuccessful, a possible solution to the problem would be treatment of the absorber solutions containing chlorite with hypochlorite or chlorine to form a solution containing chlorate and chloride, followed by conventional electrolysis in a chloride-chlorate type cell.

In the series of preliminary experiments, solutions of sodium chlorite and sodium hypochlorite (also containing sodium chloride, since the solution was prepared by passing chlorine gas into sodium hydroxide solution) were adjusted to pH values of about 6, 7, 8, 10 and 12. Then the solutions were mixed in quantities such that stoichiometric amounts of sodium chlorite and sodium hypochlorite were present. The resulting solutions after standing overnight were evaporated to a white solid on a steam bath using vacuum.

X-ray analysis of the five runs indicated incomplete reaction, since NaCl, NaClO₂ and NaClO₃ were present in the final product. Evidently an equilibrium condition existed:



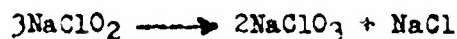
An excess of sodium hypochlorite might give more chlorate, consuming all of the chlorite.

Since electrolysis of absorber solutions in a chlorate-type cell has proven successful, further effort in this direction was abandoned.

c. Catalytic Disproportionation of Sodium Chlorite to Sodium Chlorate and Sodium Chloride

Richard W. Brown (2) reported that aqueous chlorine dioxide hydrolyzed into chloric and hydrochloric acids at 96.5°C. when a catalyst was present. These catalyzed aqueous chlorine dioxide solutions became stable after about 16 hours at 96.5°C. (about 40% hydrolyzed). The catalyst apparently is produced by overheating an impure grade of potassium chlorate when preparing chlorine dioxide by the reaction of chlorate and oxalic acid.

It was thought that perhaps sodium chlorite could be catalytically disproportionated into sodium chlorate and sodium chloride at about 100°C.:



Some exploratory test tube experiments were tried, adding various metallic ions to a sodium chlorite solution of known concentration, but no experimental data of any value was obtained.

Further study in this direction was abandoned, since electrolysis of absorber solutions in a chlorate-type cell has proven successful.

6. Large Scale Laboratory Preparations with Packed Column Reactor, and Projected Cyclic Process

a. Large Scale Laboratory Preparations

Following the procedure developed for carrying out the disproportionation of sodium chlorate with 83% sulfuric acid as outlined at the end of part 2(b) of the Laboratory Study section of this report, two large laboratory scale runs (#111 and #113) were made in each of which the charge was one pound (460g.) of sodium chlorate. Tables XIX and XX show the complete data and results of these experiments. The conversions of sodium chlorate to perchlorate were respectively 24.5% and 29.9%, and the absorbed off-gases contained respectively 90.6% and 91.6% chlorine dioxide, (9.4% and 8.4% Cl_2), showing a high level of recovery of oxidizing values. Table XVIII and part 5 of the Laboratory Study section of this report give the details of the successful chlorate cell electrolyses of these caustic solution absorbed off-gases to reform sodium chlorate which would be recycled in a continuous process.

The recovery of perchlorates from the product solutions of these runs is covered in part 4 of the Laboratory Study section of this report under Modifications #3 to #6 of the ammonium and potassium perchlorate precipitation methods. By the preferred method, product solution perchlorate was precipitated with 4 to 10% excess potassium sulfate giving an 88% recovery of potassium perchlorate.

TABLE XIX

LARGE SCALE LABORATORY DISPROPORTIONATION OF NaClO_3
WITH 83% H_2SO_4 - DATA

Exp. No.	Column Charge			Charging Rate ml./min.	Ave. Temp. of External Wall at Mid-point of Reactor-°C.	H_2 Flush Rate l./min.	Wt. or Mol. % Conversion of NaClO_3 to NaClO_4	% Recovery of NaClO_3 Charge	Oxidizing Level of Absorber Solns. NaClO_4 (No NaClO_2) 100% NaClO_4	Total Chlorine Compd. Rec. in Absorber Soln. as % of Charge (No NaClO_4) %	Composition of Absorbed Off-Gases Expressed as:	
	NaClO_3 Soln. ml.	83% H_2SO_4 ml.	Total NaClO_3 Mixed Vol. ml.								Wt. % Cl_2	Wt. % ClO_2
111(1st Pass)	728	2140	2868	460	5.5	109	0.5					
	632 g/l		2300-filtrate									
111(2nd Pass)			872g. ppt.		6.0	150	0.5	24.5	90.1	86.9	64.7	9.4
			2275									90.6
113(1st Pass)	701	2140	2841	460	6.1	108	1.0					
	(656 g/l)		2380-filtrate									
113(2nd Pass)			856.3		6.6	149.5	1.0	29.9	100.8	88.1	70.2	8.4
			2385									91.6

NOTES: (1) Nitrogen flushing gas was saturated with H_2O at 50°C., and heated to 100°C. before introduction into the bottom of the column.

(2) Weight ratio of $\text{H}_2\text{SO}_4/\text{NaClO}_3 = 6.8$

(*) Actual temperature of acid-chlorate solution within packed column reactor was approximately 40°C. below this outside wall temperature.

TABLE XI

LARGE SCALE LABORATORY DISPROPORTIONATION OF NaClO_3
WITH 83% H_2SO_4 -ANALYTICAL RESULTS

Exp. No.	Product Analysis		Wash Soln. Anal.		Absorber Soln. Analysis						Bisulfate Filter Cake Analysis				
	NaClO ₃ g.	NaClO ₄ g.	NaClO ₃ g.	NaClO ₄ g.	NaCl g.	NaClO g.	NaClO ₂ g.	NaClO ₃ g.	NaClO ₄ g.	NaClO ₃ g.	NaClO ₄ g.	NaHSO ₄ g.	H ₂ SO ₄ g.	H ₂ O (by diff.) g.	
111 (2nd Pass)	3.61	128.8	1) 0.04 2) 0.0	1.02 0.05	(1-3) 16.77 (4-5) 8.15 (6) --	0 2.51 --	72.0 16.30 --	119.4 25.7 trace	0 0 --	0.4	5.6	348	413	105	
113 (2nd Pass)	4.09	156.5	1) 0.02 2) 0.01	1.45 0.11	(1-3) 10.88 (4-5) 17.3 (6) --	0 0 --	77.2 9.88 --	123.7 44.5 .57	0 0 --	1.8	3.0	397	350	104.5	

* NOTES: 1. The NaOH solutions containing the absorbed off-gases were combined as follows.

(a) Absorbers 1 to 3 in which the NaOH was practically consumed by absorbed acid gases were combined.

(b) Absorbers 4 and 5 which were only partially saturated were combined.

(c) Absorber 6 containing only traces of off-gases was analysed in one step for all components from NaCl to NaClO_3 , and the result expressed as equivalent NaClO_3 .

2. The NaHSO_4 and H_2SO_4 values in the bisulfate filter cake were calculated from sodium and sulfate ion results.

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Material balances were made on these two runs to show a breakdown of the consumption and loss of sodium chlorate in the process.

The results are tabulated in Table XXI, and show that the total consumption and loss of sodium chlorate was 1.7 to 2.2 Kg. for each kilogram of sodium perchlorate produced. Of this amount, 1.16 Kg. NaClO_3 was theoretically required. The smaller losses in Experiment #113 represent improved operational techniques over Experiment #111, and more nearly indicate what might be expected in large scale operations.

b. Projected Cyclic Process and Cost Estimate

Preliminary to the preparation of the cost estimate, it was necessary to prepare on paper a projected cyclic process based on batch operation data with the packed column reactor. Figure No. 3 shows this projected cyclic process based on the data of experiment #111. A somewhat more efficient process would have resulted from the higher yield data of experiment #113 which, however, were not available at the time. Thus, the process shown and the cost estimate based upon it may be considered to be on the conservative side.

A cost estimate on the disproportionation process based on the results of experiment #111 was prepared. The estimate was made on the basis of a plant producing 10,000 tons per year of potassium perchlorate. A total cost of 20.2¢/lb. KClO_4 was found by the disproportionation process as compared to 14.0¢/lb. KClO_4 by the electrolytic process using platinum anodes. Details are given in Appendices A and B of this report.

At the conclusion of this research, a request was received from ONR for a cost estimate based on recovering ammonium perchlorate product. The solubility of ammonium perchlorate is greater than potassium perchlorate, and so its recovery by precipitation from the disproportionation product solution would not be as efficient. Therefore, it was concluded that the most practical and economical method would be to first remove 95% of the perchlorate from the disproportionation product solution as perchloric acid, by vacuum distillation, (see Page 33), and then react the recovered 42% perchloric acid with anhydrous ammonia. The pure ammonium perchlorate would then be completely recovered by evaporating the solution to dryness. Based on this recovery method, the cost of ammonium perchlorate when produced in a 10,000 ton per year plant was found to be 21.5¢ per lb. NH_4ClO_4 . Details of the cost estimate are given in Appendix C of this report. An outline of this procedure for the recovery of ammonium perchlorate product in the acid disproportionation process is shown in Figure 4, and is based on the same scale of operation as the cyclic process shown in Figure 3 with changes only in the treatment of the product solution.

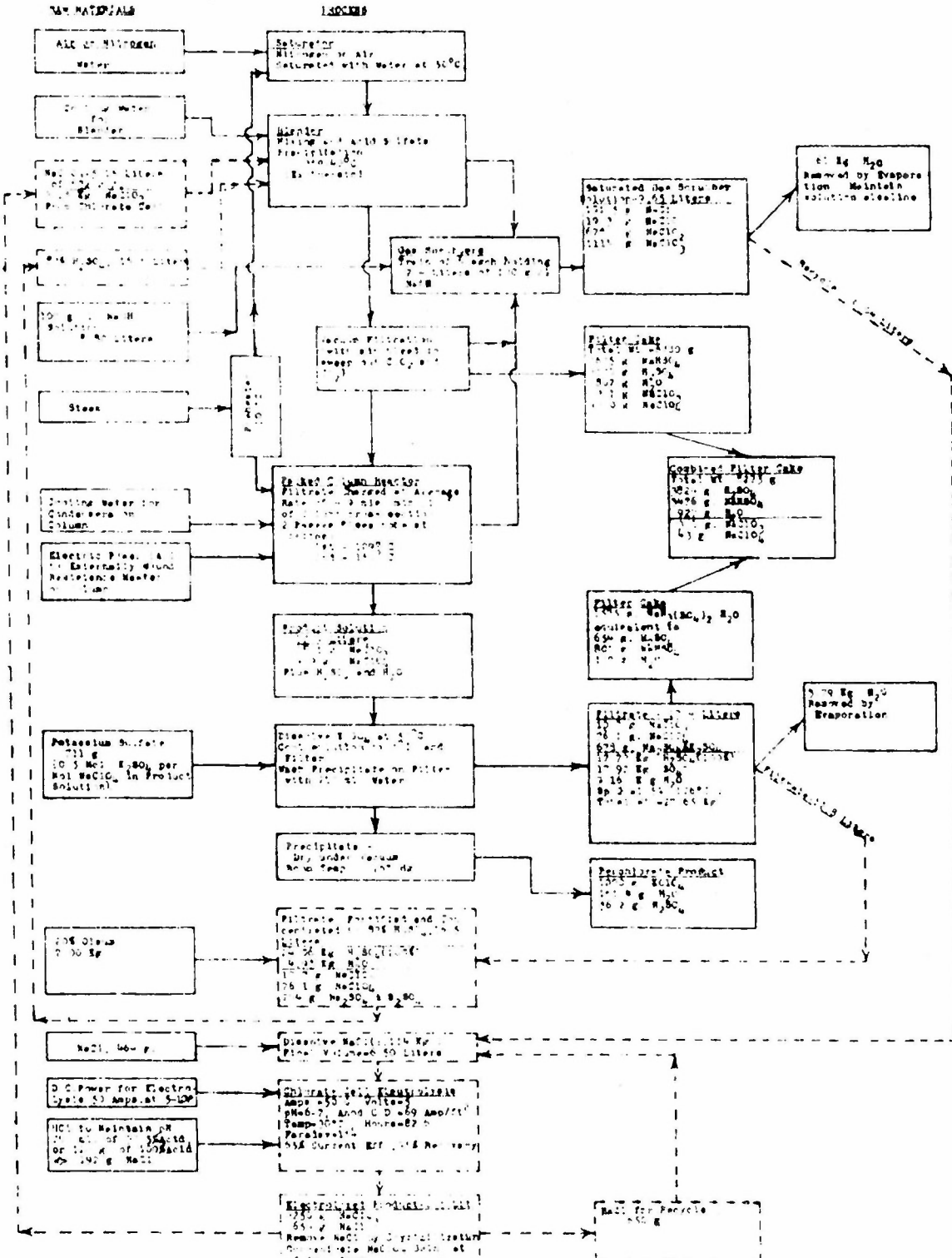
TABLE XXI

MATERIAL BALANCE ON SODIUM CHLORATE IN ACID
DISPROPORTIONATION PROCESS

BASIS - 1 Kg. Sodium Perchlorate (NaClO_4)
Produced

	EXPERIMENT NO.	
	111	113
Product - NaClO_3 consumed in forming NaClO_4 , Kg.	1.16	1.16
Process Loss, decomposition of ClO_2 and handling, Kg.	1.05	0.55
Recovery, ClO_2 off-gases and unreacted NaClO_3 , Kg.	1.36	1.23
Charge, sum of NaClO_3 in Product, Process Loss and Recovery, Kg.	3.57	2.94

FIGURE 2
PROJECTED THERM PROCESS FOR ACID DISPROPORTIONATION
OF SODIUM CHLORATE -
POTASSIUM PERCHLORATE AS PRODUCT



*Designated temperatures are external wall temperatures at mid-height of room. Internal average temperature is about 40°C above.

FIGURE 4

RECOVERY OF AMMONIUM PERCHLORATE IN THE ACID DISPROPORTIONATION PROCESS

Material to be Processed

Product Solution (Produced by cyclic process shown in Figure 3)

Volume - 17.4 liters

28 g. NaClO_3

999 g. NaClO_4

17.73 Kg. H_2SO_4 (100%)

9.16 Kg. H_2O

Objectives

Remove 95% of the perchlorate as perchloric acid by vacuum distillation at 27 inches mercury. React the recovered perchloric acid with anhydrous ammonia to form ammonium perchlorate.

Process Details

1. At a vapor temperature of 40°-50°C. (86°-112°C. pot temperature), 5.44 Kg. water are collected in the receiver and cold trap. Cold trap and receiver are drained, and pot temperature raised.
2. At a vapor temperature of 92°-116°C. (128°-196°C. pot temperature), a perchloric acid cut is collected in the receiver. The volume is 1430 ml., weighing 1865 g. and analyzing 41.6% HClO_4 , or 777 g. HClO_4 . 409 ml. water are collected at the same time in the cold trap.
3. The residue in the distilling pot then is
Volume - 11.0 liters
28 g. NaClO_3
50 g. NaClO_4
17.35 Kg. H_2SO_4
2.22 Kg. H_2O
.55 Kg. Na_2SO_4

As this residue is cooled to room temperature, a precipitate of 865 g. $\text{NaH}_3(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ is formed. This acid sulfate precipitate is filtered off and combined with a similar filter cake obtained on the mixing of 83% sulfuric acid and sodium chlorate solution.

4. The acid filtrate
Volume - 10.5 liters, approx. 89% H_2SO_4
28 g. NaClO_3
50 g. NaClO_4
16.81 Kg. H_2SO_4
2.15 Kg. H_2O
.29 Kg. Na_2SO_4

is combined with 7.55 Kg. 96% H_2SO_4 (66°Bé) and 2.48 Kg. water to form 16.5 liters of 83% sulfuric acid for recycle in the disproportionation process.

5. Ammonium perchlorate is formed by bubbling 138.3 g. (5% excess) anhydrous ammonia through the 41.6% perchloric acid, and evaporating the solution to dryness to form 909 g. ammonium perchlorate product.

SECURITY INFORMATION

TABLE XXII

SOLUBILITY OF SODIUM SULFATE IN SULFURIC ACID
AND WATER AT 25°C. (12)

Basis - 1000 grams of the solution contain:

Mols SO ₃ (or H ₂ SO ₄)	Mols Na ₂ SO ₄	Solid Phase
5.91	0.409	NaHSO ₄
6.30	0.332	"
6.64	0.297	NaHSO ₄ + NaH ₃ (SO ₄) ₂ ·H ₂ O
6.90	0.173	NaH ₃ (SO ₄) ₂ ·H ₂ O
7.36	0.071	"
7.74	0.047	"
7.82	0.044	"
8.12	0.037	"
8.29	0.042	"
8.40	0.046	"
8.70	0.076	"
8.86	0.156	"
8.93	0.259	"
8.93	0.269	"
8.93	0.273	"
8.84	0.527	" (Unstable)
8.73	0.681	" (Unstable)
8.70	0.808	" (Unstable)
8.62	0.834	" (Unstable)
8.62	0.844	" (Unstable)
8.61	0.899	" (Unstable)
8.87	0.445	NaH ₃ (SO ₄) ₂ ·H ₂ O + Na ₂ SO ₄ ·4-1/2H ₂ SO ₄
8.93	0.437	Na ₂ SO ₄ ·4-1/2H ₂ SO ₄
9.08	0.394	"
9.36	0.425	"

It is recognized that potassium perchlorate could also be produced by reacting potassium hydroxide with perchloric acid which had been vacuum distilled from the disproportionation product solution. Just as for ammonium perchlorate above, this potassium perchlorate would be free of sulfate and require no further processing other than evaporation of the solution to dryness. The cost of potassium perchlorate by this recovery method is estimated to be no higher than by precipitation from the product solution.

A necessary requirement for a workable cyclic process is the recovery and recycling of the sulfuric acid solution remaining after precipitation of the product perchlorate as the ammonium or potassium salt. A possible build-up of the concentration of sodium ion brought in with the sodium chlorate would have made necessary the discarding of all or part of this acid filtrate. However, due to the fortuitous minimum solubility of sodium sulfate in sulfuric acid solutions in the concentration range used in the disproportionation process, only a minor amount of sodium ion remained in the acid filtrate after product recovery. A large amount of the sodium was removed in the bisulfate-acid filter cake formed in the initial mixing of 83% sulfuric acid and sodium chlorate solution (650g./l.). An additional amount of sodium is removed in the projected cyclic process as a bisulfate-acid precipitate when the acid filtrate from the perchlorate product is reconcentrated by partial water evaporation prior to reformation with 20% oleum. Table XXII gives the solubility of sodium sulfate in sulfuric acid and water at 25°C. The concentration of sulfuric acid at various stages in the disproportionation process when starting with 83% sulfuric acid falls in the range of 6.9 to 8.2 mols. H_2SO_4 per 1000 grams of solution, in which range the corresponding solubility of sodium sulfate is 0.17 to 0.04 mols per 1000 grams of solution. 0.04 mols Na_2SO_4 per 1000 grams of solution is the point of minimum sodium sulfate solubility.

c. Safety Precautions

Safety precautions must be a prime consideration in carrying out the acid disproportionation process, especially on a commercial scale. Foolproof measures must be taken to prevent the formation of explosive concentrations of chlorine dioxide in the vapor state and high concentrations in the acid-chlorate solution. The literature has no statement on the explosive nature of aqueous chlorine dioxide solutions in the presence

of other substances. In this laboratory (4), no explosions were observed when aqueous solutions of chlorine dioxide ranging from 25 to 50% were tested for stability by adding various organic substances, hydrogen peroxide, 10% ferric chloride solution and concentrated hydrochloric acid, and also by subjecting the chlorine dioxide solutions to ultra-violet rays. However, chlorine dioxide solutions may still be potentially dangerous, and high concentrations should be avoided.

The chlorate solution should be added in a slow drip to concentrated sulfuric or other acid with a continuous bubbling and flushing of air or other inert gas through the solution to sweep the chlorine dioxide as fast as formed out of the reactor vessel. In event of stoppage of gas flushing for any reason, there should be provision for automatic opening of the vessel to a vent stack and a copious auxiliary supply of flushing gas through the reactor solution. The mixing of chlorate and acid solutions should preferably be carried out in a series of relatively small reactors rather than in one large vessel. Glass or ceramic lined equipment is recommended in preference to any of the common metals. Linings of certain of the inert plastic materials might prove practical.

High concentrations of chlorine dioxide gas are known to be violently explosive. It is industrial practice to maintain the partial pressure of chlorine dioxide below 30 mm. of mercury by diluting the gas as formed with air. The industrial handling of chlorine dioxide at this dilution has been reported (5) quite safe. Therefore, in any of the operations of the disproportionation process, such as mixing, filtering, or column percolation, provision must be made for adequate dilution of the released chlorine dioxide gas with a flushing stream of air or other inert gas.

All chlorine dioxide containing gas streams should be passed through caustic absorbing solutions of 100 to 200 grams NaOH per liter. Warning of an approaching chlorine dioxide saturation of the absorber solution is given by the appearance of successively darker shades of amber color. When the solution has reached a moderate but not dark amber color, it should be removed from the train of absorbers. Acid or neutral solutions of chlorine dioxide are unstable and possibly explosive, therefore, the pH of the saturated absorber solution should be immediately checked and adjusted to pH8 or higher. Continuous pH measurement of the caustic absorber solutions and their removal from the train at pH8 to 9 would be preferable on an industrial scale.

B. Background Information

1. Literature Survey

The decomposition of chlorates by strong acids has been known for many years, but very little study has been given to the reaction. Following the early observations of Stadion, Penny and Millon in the early 1800's, no work appears to have been done until 1922 when Lenhar, Stone, and Skinner (6) studied the action of a number of acids. The reaction with sulfuric acid was reported to yield perchlorate and oxides of chlorine (principally the tetroxide). It was stated that this reaction could be carried out without danger by adding the sulfuric acid slowly and preventing the reaction mixture from becoming warm. Yields with various acids were given as follows:-

H_2SO_4 conc., 50 cc./2-5g. KClO_3 , 5 hrs. - 11%

HNO_3 conc., repeated evap. on steam bath - 30%

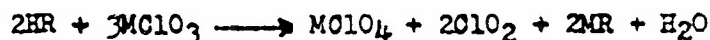
H_3PO_4 , 85%, boiled - 15%

CrO_3 with enough water to effect solution - 11%

Formic acid) decomposed KClO_3 but
Trichloroacetic acid)
Hydrofluoric acid) yielded no perchlorate
Hydrochloric acid)

Chloric acid)
Persulfuric acid)
Permanganic acid, 20%)
Arsenic acid, 50%) did not decompose KClO_3 at
Acetic acid, glacial or dilute) the boiling temperature
Monochloroacetic acid)
Oxalic acid, saturated)
Tartaric acid, 25%)
Lactic acid, 25%)

Hampel, in U.S. Patents 2,489,571 through 2,489,575 (1), discloses a cyclic process for producing perchlorates and chlorites of different metals by the action of a mineral acid (H_2SO_4 , HNO_3 , H_3PO_4 , HClO_4 , H_2SiF_6 or HF) on a chlorate in a chloride-free medium. The basic reaction (M =metal, R =acid radical) is

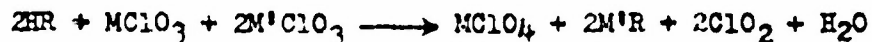


In this reaction the yield of perchlorate, in the case of the sodium salt, would be $\text{NaClO}_4/3\text{NaClO}_3 = 38.3\%$, equivalent to a 33.3 weight or mol percent conversion of sodium chlorate to perchlorate. However, the chlorine dioxide can be absorbed in an alkaline solution as follows:

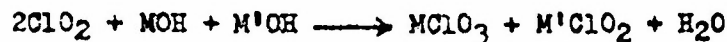


Thus, one mole of chlorate is recovered and the overall yield of sodium perchlorate would be $\text{NaClO}_4/2\text{NaClO}_3 = 57.4\%$, equivalent to a 50 weight

or mol percent conversion of sodium chlorate to perchlorate. By a proper choice of acid and by using the chlorates of two metals in the proper proportions, the separation of the perchlorate from the other salt formed can be readily accomplished on the basis of difference in solubility.



A similar expedient can be used in the chlorine dioxide absorption.



In this process, the excess acid required for the chlorate decomposition would have to be recovered and reconcentrated; and since 33% of the chlorate is not converted to perchlorate, a market or use for the chlorite would have to be developed.

In a later series of patents, issued to the Cardox Corporation, C.A. Hampel and W.L. Norem (7) in reacting $NaClO_3$ and $KClO_3$ with H_2SO_4 to form $KClO_4$, ClO_2 and $NaHSO_4$, separated the latter solid components by filtration from the reaction liquid, then treated the solid components with a limited amount of H_2O at 25° to dissolve the $NaHSO_4$ and recover the solid $KClO_4$. The filtrate is cooled to 6° , whereby $Na_2SO_4 \cdot 10H_2O$ is crystallized out. The mother liquor may be treated with Na_2CO_3 or $NaOH$ to convert the residual H_2SO_4 to Na_2SO_4 for recycling or evaporated to recover H_2SO_4 in a concentrated form.

C.A. Hampel recovered the chlorine values by reacting chlorine dioxide with equivalent amounts of KOH and $NaOH$ and obtained $KClO_3$ and anhydrous $NaClO_2$ by suitable crystallization procedures (8); or by reacting chlorine dioxide with $NaOH$ and KCl to obtain $KClO_3$, $NaCl$ and anhydrous $NaClO_2$ (9); and by reacting chlorine dioxide with a mixture of lime, K_2SO_4 and Na_2SO_4 to obtain $KClO_3$ and a mixture of 95% $NaClO_2$ and 5% $CaSO_4$ (10).

A continuous cyclic process in which a mixture of sulfuric acid and sodium chlorate was reacted at a temperature between 55° and $60^\circ C$. primarily to produce chlorine dioxide weak in chlorine rather than perchlorate was recently disclosed in the German Patent No. 878,486 issued to Max Audoynaud (11). Since the object of this invention was to produce chlorine dioxide by bubbling a finely dispersed air or inert gas stream through the chlorate-sulfuric acid solution rather than to produce perchlorate, no figures were given on perchlorate yield. However, it was stated that for decomposing 531.8 kg. of sodium chlorate, 953 kg. of H_2SO_4 (100% basis) was consumed producing 226.7 kg. of ClO_2 (96%) and 10.2 kg. of Cl_2 (4%). The percentage of chlorate transformed into chlorine dioxide was 67.5%.

The conditions and yields for this process correspond closely to those found for the acid disproportionation method for perchlorate. The H_2SO_4 (100%)/ $NaClO_3$ ratio for material consumed for the German process is thus $\frac{953}{531.8} = 1.79$ where in this work the corresponding ratios found were 1.48 and 1.53 in large scale laboratory experiments. The percentage of chlorate transformed into chlorine dioxide was 67.5% in the German

process; in this work the maximum percentage amounted to 62%. (See part 6 of the Laboratory Study section of this report.)

2. Patent Situation

A patentability and infringement study was completed on the projected process which is a cyclic process for acid disproportionation of sodium chlorate producing potassium perchlorate or ammonium perchlorate.

In the projected process, sodium chlorate and 83% sulfuric acid are mixed in a blender, sodium acid sulfate being precipitated. The resulting mixture is subjected to vacuum filtration, with an air bleed to sweep out chlorine dioxide and chlorine, and a filter cake containing predominantly sodium acid sulfate and sulfuric acid is removed. The filtrate is then passed through a packed column reactor in two passes, utilizing a temperature of about 70°C. on the first pass and 110°C. on the second pass. The product solution is essentially a solution of sodium perchlorate, to which potassium sulfate is added, resulting in the precipitation of potassium perchlorate, which is the desired product.

In an alternative embodiment, the product solution may be subjected to vacuum distillation, resulting in removal of 95% of the perchlorate as perchloric acid, which is then reacted with anhydrous ammonia to form substantially pure ammonium perchlorate.

The off-gases from the blender are absorbed in sodium hydroxide solution to produce a saturated gas scrubber solution containing sodium chloride, sodium hypochlorite, sodium chlorite and sodium chlorate, this mixture being subjected to chlorate cell electrolysis, with additional salt, to produce an electrolyzed product containing sodium chlorate and sodium chloride. The sodium chloride is removed from the electrolyzed product by crystallization, and the sodium chlorate is concentrated and recycled to the blending step.

No question of infringement of any unexpired U. S. patents appears to be involved in the operation of this process or in any of the component parts thereof, with the exception of the patent to Audoynaud, No. 2,641,528, assigned on its face to Mathieson Chemical Corporation, which discloses and claims a process of producing chlorine dioxide which comprises passing a current of finely divided inert gas into a solution warmed to about 55-60°C. and consisting essentially of metallic chlorate in a concentrated mineral acid, which may be sulfuric acid, and recovering the resulting chlorine dioxide which has been released and removed from the solution by the action of the current of finely divided inert gas. While the temperature in the blender in the projected process is stated to be 35-40°C., it is not believed that this temperature difference would avoid infringement of the Audoynaud patent unless the patentee took a position during prosecution of his application which is inconsistent with a broadening of the temperature range in the claims to include the range of 35-40°C. However, the patent to Audoynaud presents no bar to the operation of the process. Thus, it is disclosed in the patent to Hampel, No. 2,489,571, assigned on its face to Cardox Corporation, that an inert gas is passed through a reaction chamber in which chlorate decomposition is being carried out in order to remove chlorine dioxide from the reaction zone. The gas may be, e.g., air or nitrogen. Hampel also discloses that the temperature should be kept below about 70°C., as above this temperature chlorine dioxide may begin to

decompose thermally, and also discloses that although the decomposition temperature will vary with the concentration of the chlorine dioxide in the carrier gas, the lower the concentration, the higher the safe temperature limit. Hampel states further that the useful temperature range is from 0°C. to about 70°C., the rate being about four times as great at 60°C. as it is at 25°C. Unless the patentee, Audouyoud (a resident of France), can show an invention date in the United States prior to February 12, 1946, the filing date of the Hampel patent, it is believed that the Hampel patent constitutes an anticipation of the Audouyoud disclosure and claims and that the latter is therefore invalid.

The most pertinent patent discovered, as regards the entire process, is the Hampel patent aforementioned, which discloses a cyclic process for producing perchlorates and chlorites of different metals, in which either two chlorates or one chlorate and another salt are reacted with an acid, which may be sulfuric acid, while an inert gas, as previously noted, is passed through the reaction chamber in which the chlorate decomposition is being carried out. The patentee discloses that the acid may be all fresh acid or part of it may be obtained by regeneration within the system. A high acid concentration is indicated in view of the statement that the reaction will nearly cease if the concentration is below 60% and, in certain of the examples, sulfuric acid of 85% concentration is employed. The temperature, as previously noted, is kept below 70°C. due to the adverse effects upon chlorine dioxide resulting from operation above this temperature.

The patentee also discloses the separation of perchlorate from the salt which is formed with the acid radical and states that sufficient water may be added to bring in solution all of the more soluble ones of these products, the insoluble product then being separated by simple filtration or centrifuging.

The chlorine dioxide produced is reacted with an alkaline material in an aqueous medium to form a chlorate and a chlorite, this operation being generally performed by passing the chlorine dioxide gas through a water solution of the alkali, a suitable initial concentration of alkaline compound being approximately 15% by weight. The patentee further states that the quantity of absorbing medium required may be changed by varying the temperature, the liquor circulation rate, the time of contact between the gas and the absorbing medium, and the concentration of the alkaline material in the absorbing medium.

As previously noted, the Hampel patent presents no question of infringement, since each of the claims requires the presence of a third reactant in addition to a strong mineral acid and a metal chlorate.

The patent to Hampel et al., No. 2,496,287, assigned on its face to Cardox Corporation, is of interest in connection with the step of precipitating sodium acid sulfate in the blender. This patent relates to a process for separating chemical compounds in which the components to be separated are sulfuric acid, potassium perchlorate and sodium acid sulfate. The process involves filtration of a slurry containing the three components to remove the excess sulfuric acid, the filter cake being transferred to a washer in which it is treated with water in an amount sufficient to dissolve all

of the sodium acid sulfate contained in the cake. The slurry of solid potassium perchlorate in a solution of sodium sulfate and potassium perchlorate in dilute sulfuric acid is filtered, whereby the solid potassium perchlorate is separated for drying. In view of the known solubilities of potassium perchlorate and sodium perchlorate, it is believed that no invention would be exercised in maintaining sodium perchlorate in solution and separating sodium acid sulfate by filtration, this conclusion being fortified by the disclosure of the Hampel patent No. 2,489,571.

The patent to Given, No. 1,273,477, assigned on its face to Atlas Powder Company, is of interest in connection with the step of vacuum distillation of the product solution to produce a perchloric acid which is then reacted with ammonia to form ammonium perchlorate. The Given patent relates to a method of producing ammonium perchlorate in which a soluble perchlorate salt is treated with ammonia gas in the presence of carbon dioxide. If one skilled in the art would know, as a result of this disclosure, that a pure perchloric acid could be reacted with ammonia to produce a pure ammonium perchlorate, then it is believed that the Given disclosure constitutes an anticipation of any novelty which may reside in this step, although it is not intended that any inference of patentability be drawn from the absence of more pertinent patent literature, since it is believed that the reaction of perchloric acid with ammonia to produce ammonium perchlorate is obvious.

The patent to Schumacher, No. 2,511,516, assigned on its face to Western Electrochemical Company, and the patent to Vanharen et al., No. 2,584,824, assigned on its face to Solvay & Cie, are of interest in connection with the electrolysis of the saturated gas scrubber solution, the former patent disclosing and claiming the improvement in a process for making sodium chlorate by the electrolysis of an aqueous solution containing sodium chloride and a small amount of sodium chromate, which consists of continuously withdrawing electrolyte from an electrolytic cell, continuously passing into the electrolytic cell an electrolyte consisting of the mother liquor from the said withdrawn electrolyte, after cooling to remove the excess sodium chlorate, and containing not less than 75 grams per liter of sodium chloride together with not less than about 400 grams of sodium chlorate per liter, the electrolyte having a pH of about 6.1, and electrolyzing the circulating electrolyte to produce additional sodium chlorate. The latter patent discloses and claims the process of preparing an alkali metal chlorite which comprises subjecting to electrolysis as a catholyte in a diaphragmed electrolytic cell an aqueous solution comprising an alkali metal hydroxide, and simultaneously introducing chlorine dioxide into direct contact with the polarized cathode in a quantity stoichiometrically in excess of the hydrogen discharged at the cathode, while maintaining the catholyte slightly acid to nearly neutral, thereby obtaining the chlorite.

The patent to Cunningham, No. 2,169,066, assigned on its face to The Mathieson Alkali Works, Inc., is of interest in connection with the absorption of off-gases from the blender in sodium hydroxide solution, the patent disclosing that chlorine dioxide is absorbed in an aqueous solution containing sodium hydroxide in suitable amount until the solution is substantially neutral, this step being incidental to the preparation and separate recovery of sodium chlorate and sodium chlorite.

The following patents are of general interest:

<u>Patent Number</u>	<u>Date</u>	<u>Inventor</u>	<u>Assignee</u>
2,280,938	4/28/42	George P. Vincent	The Mathieson Alkali Works, Inc.
2,489,572	11/29/49	Clifford A. Hampel	Cardox Corporation
2,489,573	11/29/49	Clifford A. Hampel	Cardox Corporation
2,489,574	11/29/49	Clifford A. Hampel	Cardox Corporation
2,489,575	11/29/49	Clifford A. Hampel	Cardox Corporation

From the foregoing, it is apparent that there is little novelty in the projected process. It may, however, be possible to obtain limited patent coverage of the process as a whole by including specific limitations in the claims, which might influence the Patent Office to allow them. It is also obvious, however, that no broad patent coverage can be obtained in this case.

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- (11) German Patent 878,486 (June 5, 1953), Max Audoynaud
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Z. anorg. 61, 92 (1909)
Z. anorg. 80, 236 (1913)
- (13) Haller, J.F., and Listek, S.S., Anal. Chem. 20, 639-42 (1948)

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RESEARCH NOTEBOOK RECORDS OF EXPERIMENTAL WORK

1217: p. 103-195
1258: p. 23-200
1289: p. 4-193
1364: p. 25-29, 84-119
1365: p. 1-199
1367: p. 1-175
1433: p. 1-65

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SECRET
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APPENDIX

A. Cost Estimate on Potassium Perchlorate by The Electrolytic Method

SUMMARY SHEET

Estimated Manufacturing Cost of 10,000 TPY Potassium Perchlorate

Direct Cost

Including raw materials, labor, maintenance, utilities
and processing cost for sodium perchlorate 13.7¢/lb.

Indirect Cost

Including plant overhead (superintendent, shift supervisors,
chemists, office workers, plant guards, etc.) 0.3¢/lb.

Total Cost

Not including administrative overhead and fee of the operator,
or depreciation, taxes and insurance 14.0¢/lb.

Process

Sodium chlorate liquor is fed batchwise to electrolytic
cells employing copper anodes plated with platinum. The
product of electrolysis, sodium perchlorate, is converted
to the potassium salt by the addition of a hot, concentrated
solution of potassium chloride. The product is then cooled,
crystallized, filtered, and dried.

Investment Cost

Sodium Perchlorate Plant	\$2,570,000
Potassium Perchlorate Plant	<u>2,120,000</u>
Total	\$4,690,000

Productive Capacity

The potassium perchlorate plant is based on a production
of 10,000 TPY. The sodium perchlorate capacity is keyed
to the production of potassium perchlorate.

Probable Accuracy of Estimate

This estimate is believed to have an accuracy of $\pm 20\%$.

B. Cost Estimate on Potassium Perchlorate by The Acid Disproportionation Process

SUMMARY SHEET

Direct Cost

Including raw material, labor, maintenance, utilities
and processing cost for sodium chlorate 24.0¢/lb.

Indirect Cost

Including plant overhead (superintendent, shift supervisors,
chemists, office workers, plant guards, etc.) 1.2¢/lb.

By-Product

Sodium bisulfate and sulfuric acid by-products are credited
for the equivalent sulfuric acid at \$19 per ton of sulfuric
acid 5.0¢/lb.

Total Cost

Not including administrative overhead and fee of the operator,
or depreciation, taxes, and insurance 20.2¢/lb.

Process

Sodium chlorate produced by the electrolysis of sodium chloride (NaCl) and recycle sodium hypochlorite (NaClO) and sodium chlorite (NaClO₂) is mixed with 83% sulfuric acid for six hours at 40°C. with the continued injection of 50°C. moist air. The formed sodium bisulfate-sulfuric acid is removed by filtration. The filtrate is heated in a packed column to 70°C. The effluent chlorine dioxide gas stream from the blenders, filters and strippers is reacted with dilute caustic soda and recycled to the sodium chlorate cells after partial evaporation.

The liquor from the stripper is reacted with potassium sulfate at 50°C. The products of reaction are cooled to 2°C. and filtered. The filtrate is partially evaporated, mixed with oleum to obtain 83% sulfuric acid and returned to the blenders. The formed potassium perchlorate is then vacuum dried and prepared for sale.

Investment Cost

Sodium Chlorate Plant	\$5,300,000
Sulfuric Acid Plant	1,100,000
Potassium Perchlorate Plant	<u>5,453,000</u>
Total	\$11,853,000

By-Product

The acid disproportionation method produces a mixed filter cake of about 3.5 pounds of sodium bisulfate and 3.8 pounds of sulfuric acid per pound of product. This by-product is credited for the sulfuric acid content at \$19.00/ton.

Productive Capacity

The potassium perchlorate plant is based on a production of 10,000 TPY. The sodium chlorate, sodium perchlorate and sulfuric acid capacities are keyed to the production of potassium perchlorate.

Probable Accuracy of Estimate

This estimate is believed to have an accuracy of $\pm 20\%$.

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C. Cost Estimate on Ammonium Perchlorate by the Acid Disproportionation Process

SUMMARY SHEET

Estimated Manufacturing Cost of 10,000 TYP Ammonium Perchlorate

Direct Cost

Including raw material, labor, maintenance, utilities and processing cost for sodium chlorate 25.8¢/lb.

Indirect Cost

Including plant overhead (superintendent, shift supervisors, chemists, office workers, plant guards, etc.) 1.3¢/lb.

By-Product

Sodium bisulfate and sulfuric acid by-products are credited for the equivalent sulfuric acid at \$19 per ton of sulfuric acid 5.6¢/lb.

Total Cost

Not including administrative overhead and fee of the operator, or depreciation, taxes and insurance 21.5¢/lb.

Process

Sodium chlorate produced by the electrolysis of sodium chloride (NaCl) and recycle sodium hypochlorite (NaClO) and sodium chlorite (NaClO₂) is mixed with 83% sulfuric acid for six hours at 40°C. with the continued injection of 50°C. moist air. The formed sodium bisulfate-sulfuric acid is removed by filtration. The filtrate is heated in a packed column to 70°C. The effluent chlorine dioxide gas stream from the blenders, filters and strippers is reacted with dilute caustic soda and recycled to the sodium chlorate cells after partial evaporation.

The liquor from the packed column or stripper is vacuum distilled at 27 inches of mercury to remove 95 percent of the perchlorate content as 42% perchloric acid. The sulfuric acid residue is combined with 96% sulfuric acid and water to form 83% sulfuric acid returned to the blenders. Ammonium perchlorate product is formed by bubbling anhydrous ammonia through the 42% perchloric acid, and evaporating the solution to dryness.

Investment Cost

Sodium Chlorate Plant	\$5,600,000
Sulfuric Acid Plant	1,200,000
Ammonium Perchlorate Plant	5,900,000
TOTAL	\$12,700,000

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SECURITY INFORMATION

By-Product

The acid disproportionation method produces a mixed filter cake of about 3.9 pounds of sodium bisulfate and 4.3 pounds of sulfuric acid per pound of ammonium perchlorate product. This by-product is credited for the sulfuric acid content at \$19.00/ton.

Productive Capacity

The ammonium perchlorate plant is based on a production of 10,000 TPY. The sodium chlorate, sodium perchlorate and sulfuric acid capacities are keyed to the production of ammonium perchlorate.

Probable Accuracy of Estimate

This estimate is believed to have an accuracy of $\pm 20\%$.

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D. Analytical Procedure for Mixtures Containing Perchlorate, Chlorate, Chlorite, Hypochlorite and Chloride

This complete analytical procedure replaces a previously used procedure which covered methods for perchlorate, chlorate and chloride only, and was given in Section F of Part II of the final report on Project NR 352-263/2-19-51, which issued August 31, 1951. The present procedure is based partly on the work of Haller and Listek (13) on determination of chlorine dioxide and other active chlorine compounds in municipal water supplies. Their methods on parts per million determinations were adapted to higher concentrations. The method for sodium hypochlorite is the standard method used for analysis of an important industrial product, calcium hypochlorite. Development, testing and integration of the various individual methods into a complete procedure was done by the Analytical Section of the R. & D. Division of Pennsalt. Table XXIII gives data on the testing of this analytical procedure for the range of interest in this study, and shows analytical results duplicating actual sample composition to within 1.5% or better.

Analytical Procedure

0.0 Sample Preparation

0.1 Solids

0.11 Weight accurately approximately 6 grams of sample, dissolve in water and dilute to 500 ml. in a volumetric flask.

0.2 Liquids

0.21 Take a known volume of solution which contains approximately 6 grams of solid and dilute with water to 500 ml. in a volumetric flask.

1.0 Determination of Hypochlorite Content

1.1 Apparatus

1.11 250 ml. beaker

1.12 50 ml. buret

1.13 10 ml. calibrated pipet

1.2 Reagents

1.21 Standard 0.1 N Sodium arsenite solution

1.22 Starch - iodide test paper

1.23 Buffer solution: 100 gms. of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ plus
150 gms. of Na_2HPO_4 per liter

1.3 Procedure

1.31 Pipet 10 ml. of the sample into 50 ml. of water in a 250 ml. beaker.

1.32 Add 5 ml. of the buffer solution. Check with pH paper to make sure pH is between 6 and 7. If not, add more buffer.

1.33 Add standard 0.1 N sodium arsenite from the buret to the solution in the beaker with stirring, until a drop of the solution on the stirring rod does not yield a blue color on the starch iodide paper. Do not overrun the endpoint. Record the volume of sodium arsenite used, V.

1.4 Calculations

(V) (Normality of sodium arsenite) (0.03723) = gms. of NaOCl in aliquot taken.

2.0 Determination of Chlorite Content

2.1 Apparatus

2.11 250 ml. beaker

2.12 50 ml. buret

2.13 10 ml. calibrated pipet

2.2 Reagents

2.21 Standard 0.1 N sodium arsenite solution

2.22 Solid potassium iodide

2.23 Buffer solution - 100 gms. of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ plus 150 gms. of Na_2HPO_4 per liter

2.24 Approximately 0.5 N sulfuric acid

2.25 Starch indicator solution, 0.5%

2.3 Procedure

2.31 Add 10 gms. of potassium iodide to 50 ml. of water in a 250 ml. beaker.

2.32 Pipet 10 ml. of the sample into the beaker

2.33 Add approximately 0.5 N sulfuric acid until pH is between 1 and 2 using pH paper. Mix and let stand one minute.

2.34 Add 10 ml. of buffer solution. Check with pH paper to make sure pH is between 6 and 7. If not, add more buffer.

2.35 Titrate with 0.1 N sodium arsenite solution to disappearance of iodine color, using starch indicator, if necessary. Record the volume of sodium arsenite used, W.

2.4 Calculations

$(W-V) (\text{Normality of sodium arsenite}) (0.02261) = \text{gms. of } \text{NaClO}_2 \text{ in aliquot taken.}$

3.0 Determination of Chlorate Content

3.1 Apparatus

3.11 250 ml. iodine flask

3.12 50 ml. buret

3.13 10 ml. calibrated pipet

3.2 Reagents

3.21 Solid sodium bromide

3.22 10% potassium iodide solution

3.23 Concentrated hydrochloric acid

3.24 Standard 0.1 N sodium thiosulfate

3.25 Starch indicator solution, 0.5 percent

3.3 Procedure

3.31 Pipet 10 ml. of the sample into the 250 ml. iodine flask

3.32 Add 2 gms. of solid sodium bromide

3.33 Add 20 ml. of concentrated hydrochloric acid and stopper flask immediately. Shake and let stand 5 minutes.

3.34 Add 20 ml. of the 10% potassium iodide solution to the flask without allowing any gas to escape. Shake well.

3.35 Titrate with 0.1 N sodium thiosulfate to disappearance of iodine color, using starch if necessary. Record volume of sodium thiosulfate used, X.

3.4 Calculations

(X) (Normality of sodium thiosulfate) = E

(W) (Normality of sodium arsenite) = F

(E-F) (0.01774) = gms. of NaClO_3 in aliquot taken

4.0 Determination of Chloride Content

4.1 Apparatus

4.11 500 ml. iodine flask

4.12 50 ml. buret

4.13 25 ml. calibrated pipet

4.2 Reagents

4.21 Ferrous sulfate, hydrated, solid ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)

4.22 Sulfuric acid (1:1)

4.23 Standard 0.1 N silver nitrate solution

4.24 Standard 0.1 N potassium thiocyanate solution

4.25 Nitrobenzene, purified

4.3 Procedure

4.31 Add 5 ml. of sulfuric acid (1:1) to 150 ml. of water in the 500 ml. iodine flask

4.32 Add 10 gms. of ferrous sulfate

4.33 Pipet 25 ml. of sample into flask. If a precipitate forms, add more sulfuric acid until it dissolves

4.34 Place flask on steam bath for one hour

- 4.35 Cool, add standard silver nitrate from a buret until in excess. Record volume of silver nitrate, A.
- 4.36 Add 2 ml. of nitrobenzene and shake vigorously for 1 minute.
- 4.37 Titrate the excess silver nitrate with standard potassium thiocyanate to first permanent reddish brown color. Record volume of thiocyanate, B.

4.4 Calculations

- (A) (Normality of silver nitrate) = G
- (B) (Normality of potassium thiocyanate) = H
- (C-H) (0.03546) = gms. of chlorine from chloride, hypochlorite, chlorate and chlorite in aliquot taken = K
- (gms. of NaClO in aliquot) (0.4763) = gm. chlorine due to NaClO = L
- (gms. of NaClO₂ " ") (0.3920) = " " " " NaClO₂ = M
- (gms. of NaClO₃ " ") (0.3331) = " " " " NaClO₃ = N
- (K) - (L+M+N) = gm. of chlorine from chloride only = P
- (P) (1.6483) = gm. of NaCl in aliquot taken

5.0 Determination of Perchlorate Content

5.1 Apparatus

- 5.11 500 ml. iodine flask
- 5.12 50 ml. buret
- 5.13 25 ml. calibrated pipet

5.2 Reagents

- 5.21 Ferrous sulfate, hydrated, solid ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)
- 5.22 Sulfuric acid (1:1)
- 5.23 Titanous sulfate, 20% solution
- 5.24 Nitric acid (1:1)
- 5.25 Standard 0.1 N silver nitrate solution
- 5.26 Standard 0.1 N potassium thiocyanate solution

5.3 Procedure

- 5.31 Add 2 ml. of sulfuric acid (1:1), to 20 ml. of water in the 500 ml. iodine flask.
- 5.32 Add 2 gm. of ferrous sulfate
- 5.33 Pipet 25 ml. of sample into flask. If a precipitate forms, add more sulfuric acid until it dissolves.

- 5.34 Heat on steam bath 15 minutes.
- 5.35 Add 20 ml. of sulfuric acid (1:1).
- 5.36 Pipet 20 ml. of titanous sulfate solution into flask.
- 5.37 Place on hot plate for one hour. Keep solution at boiling, but do not boil.
- 5.38 Cool to just above room temperature and add 5 ml. of nitric acid (1:1).
- 5.39 Place on hot plate 5 minutes (solution should now be yellow colored, if still purple, add more nitric acid). Shake flask occasionally to remove oxides of nitrogen.
- 5.3.10 Cool, add standard silver nitrate from buret until in excess. Record volume of silver nitrate, C.
- 5.3.11 Add 2 ml. of nitrobenzene and shake vigorously for one minute.
- 5.3.12 Titrate the excess silver nitrate with standard potassium thiocyanate to first permanent reddish solution. Record volume of thiocyanate added, D.
- 5.3.13 Run blank on all reagents, without sample. Subtract blank from sample determination.

5.4 Calculations

- (C) (Normality of silver nitrate) = R.
- (D) (Normality of potassium thiocyanate) = S.
- (R-S) (0.03546) = gms. of chlorine from chloride, hypochlorite, chlorite, chlorate and perchlorate in aliquot taken = T.
- (T-K) = gms. of chlorine due to perchlorate only = Z.
- (Z) (3.4531) = gms. of NaClO_4 in aliquot taken.

TABLE XXIII

TESTING ANALYTICAL PROCEDURE

Sample No.	Sample Composition - g./l.				Analytical Results - g./l.				
	NaCl	NaClO ₂	NaClO ₃	NaClO ₄ · H ₂ O	NaCl	NaClO	NaClO ₂	NaClO ₃	NaClO ₄ · H ₂ O
1		11.8				None	11.7		
2			12.0			None	None	11.9	
3				10.46		None	None		10.43
4		8.0		6.1		None	{8.1 7.9		{6.0 6.0 6.0
5	3.7		6.3	4.1	{3.7 3.7	None	None	{6.3 6.3	{4.0 4.1 4.1

NOTE: A known sample of NaClO could not be prepared. In practice, analysts depend on check results with a given sample.

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